

Lion Fire: Extinguishment and mitigation of fires in Li-ion batteries at sea

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Abstract

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The shipping industry is facing increasing pressure to cut emissions. Diesel-electric hybrid or fully electrical propulsion systems can offer significant savings in fuel consumption and reduce emissions. However, the use of energy storage battery systems on board vessels is introducing new fire hazards and advice on suitable fire extinguishing systems and agents is desired. In a series of tests, both total compartment application water spray and water mist systems and direct injection (using several different agents) into the module were evaluated in fire tests conducted to compare different fire extinguishing approaches for a fire in a battery cell. A test compartment was constructed to simulate a battery room and a commercially available lithium-ion (Li-ion) battery cell was positioned inside a cubic box that mimicked a battery module. By heating the battery cell, combustible gases were generated, and these gases were ignited by a pilot flame inside the simulated battery module. The tests indicated that fire extinguishment of a battery cell fire inside a battery module is unlikely when using total compartment water spray or water mist fire protection systems. The water droplets are simply not able to penetrate the battery module and reach to the seat of the fire. Direct injection of the fire extinguishing agent inside the battery module is necessary. The tests also showed that agents such as water and low-expansion foam, with a high heat capacity, provide rapid cooling and fire extinguishment. The reduced water surface tension associated with low-expansion foam may improve the possibilities for water penetration whilst agents with a high viscosity may not be able to spread to the seat of the fire. Agents with less heat capacity, such as high-expansion foam and nitrogen gas, provide less cooling but fire extinguishment can still be achieved if designed correctly.

Key words: Lithium-ion batteries, ships, battery room, fire-fighting

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Preface

The Lion Fire @ Sea project was funded by the Swedish Maritime Administration (Sjöfartsverket) and RISE Research Institutes of Sweden which is gratefully acknowledged. Thanks are also extended to acknowledge the work and equipment provided by internal resources (in-kind) from the project partners: FiFi4Marine BV Sweden AB, Johnson Controls International, Dafo Fomtec AB, GPBM Nordic AB and the Swedish Transport Agency. The technicians at RISE Safety are acknowledged for their assistance during the tests.

Sammanfattning

För att minska emissionerna från sjöfarten kan el- eller el-hybrid-drift användas. Energilager i form av batterier utgör dock en ny form av fara som man inom sjöfarten hittills inte har behövt ta hänsyn till. Den batterityp som för närvarande är mest aktuell att introduceras på fartyg är Li-jon batterier, då dessa har många fördelar i form av hög energitäthet och lång livslängd. Dock är Li-jon batterier stabila endast inom vissa driftområden och de är även känsliga för yttre mekanisk påverkan och värme. Om batteriet hamnar utanför sitt driftområde kan det hamna i ett tillstånd av självuppvärmning, så kallad "thermal runaway", som kan orsaka brand, explosion och utsläpp av brännbara och giftiga gaser. Det är viktigt att begränsa konsekvenserna av en sådan händelse och att kunna släcka en batteribrand ombord på fartyg. Dock är kunskapen om effektiviteten av olika släckmedel och släckmetoder mot bränder i Li-jon batterier begränsad och inte allmänt tillgänglig.

Denna rapport redovisar resultat från släckförsök mot en (1) Li-jon battericell placerad i en simulerad batterimodul i ett mindre rum. Släckmedlet applicerades antingen inuti batterimodulen (punktskydd) eller i rummet (rumsskydd) och flera olika släckmedel provades. Effektiviteten utvärderas med hjälp av temperaturmätningar och videoobservationer.

Resultaten visade på vikten av att släckmedlet når fram till den brinnande cellen. Vattensprinkler eller vattendimma i rummet har ingen påverkan på branden inne i modulen eftersom vattendropparna helt enkelt inte når branden. Resultaten visade också att gasformiga släckmedel (i detta fall provades kvävgas) kan slå ner flammorna i den cell som brinner men att de inte kyler intilliggande celler, vilket gör att det kan finnas risk att dessa celler hamnar i självuppvärmning även om initialbranden har släckts.

Brandförsöken visar att vattenbaserade system (med eller utan tillsatser) monterade i en batterimodul både kan släcka en brand och kyla intilliggande celler.

Resultaten från studien är indikativa så till vida att försök endast genomfördes med en (1) Li-jon-cell. Batterimodulen designades för att simulera problemen med att distribuera och nå den brandutsatta cellen med släckmedel, men försök med en hel batterimodul skulle behöva genomföras för att korrekt återspegla verkliga installationer.

1 Introduction

Battery propulsion is an essential element for the maritime sector to reach their environmental goals. The lithium-ion (Li-ion) battery type is currently the most prominent; it has many advantages related to energy and power density but also some safety drawbacks. The electrolyte is combustible, and the cells are only thermally stable under certain operating conditions.

There is some general advice available on how safety should be ensured when using Li-ion batteries [1], but there is a lack of test methods for fire-fighting systems to be used for energy storage battery systems. There are also contradicting advices on suitable fire extinguishing agents for battery fires and therefore uncertainty regarding appropriate active fire protection systems. Some of the contradicting advices can emerge from the difficulties to distinguish between lithium-ion batteries and lithium-metal batteries, as both are often referred to as Lithium batteries. There are also contradicting advices due to the sparks etc. emerging when one is cutting a battery to reach the inside of it for extinguishing purposes, which has led to the conclusion that extinguishment should not be attempted inside of a battery casing. Tests conducted and presented publicly are often not described in significant detail. There are also commercial videos available showing the effectiveness of different extinguishing systems against a single battery cell, but seldom are comparisons made of how it would look like without the use of such a system, the extinguishment could e.g. start when the fire is about to self-extinguish as the fuel is consumed. Fire testing with batteries is expensive and it is difficult for small companies to contradict false advices or to establish a good understanding of the processes involved concerning fire extinguishment involving Li-ion batteries, which stresses the benefits of public studies addressing this item. Large companies may have very good knowledge of the processes involved and the performance of different extinguishing agent or systems, but this knowledge is usually proprietary information. The Lion Fire project was therefore initiated to provide such basic understanding of the processes involved.

The Lion Fire project involved several different fire extinguishing agents and application methods against a fire in a Li-ion battery pouch cell mounted, in a purpose-built battery module mock-up. Both the experimental set-up and the results of the tests are documented and made public through this report. The purpose was not to provide specific system design requirements or recommendations, but rather to indicate suitable systems and agents for Li-ion fire extinguishment and particularly to correct many of the common misconceptions about Li-ion fire-extinguishment e.g. regarding the use of water and how the fire-extinguishing agent should be applied. Two approaches for agent application were investigated, namely a total compartment system application with water spray or water mist in the battery room as well direct injection of the agent into the purpose-built battery module mock-up.

2 Li-ion battery fire extinguishment

Li-ion batteries have many advantages related to energy and power density but have drawbacks related to safety, as they are only stable within a limited range of operating conditions, for example within certain operating temperatures and voltages. Conditions that can bring the battery into a self-heating stage, that can develop into a so-called thermal runaway [2, 3], include overcharge, over-discharge, mechanical abuse, heating and short circuits. There is also a possibility that internal short circuiting, leading to a thermal runaway occurs due to impurities or other imperfections in the battery cells originating from the manufacturing process or dendrite build up.

A Li-ion battery cell essentially consists of anode, cathode, separator, electrolyte and packaging. There are several types of commercial anode and cathode materials which have different properties in terms of performance and safety. In case of cell overheating, the polymer separator typically melts at temperatures ranging between about 130-160 °C [4]. Without the separator there will be an internal short circuit of the battery cell, which will discharge its electrically stored energy capacity and will heat up the cell and the adjacent cells and structures in the battery pack by Joule heating. The electrical energy released in such self-heating is typically less than the combustion energy of burning of the battery cell. There are limited measurements available, but the chemical energy released in a fire can be about 5-20 times the electrical energy [5, 6, 7].

The electrolyte in Li-ion batteries consists of a Li-ion salt solved in a flammable solvent. This solvent has a boiling temperature in the range of 90-160 °C and any heating up to these temperatures will cause the solvent to evaporate. This causes the cells to swell and eventually the solvent will be released out of the cell, either because the cell is venting through the cell safety vent or because of cell rupture. The released gases are flammable and toxic [5, 6, 7, 8, 9]. The gases are either emitted as the organic solvents, such as dimethyl carbonate (DMC), diethyl carbonate (DEC), ethylene carbonate (EC), or decomposed into other gases such as CO, H₂, CH₄ etc. or blends of these gases [8, 9, 10, 11, 12, 13]. The released gases can either ignite immediately upon release, causing a flare which potentially can heat up other cells such that they are forced into thermal runaway. Alternatively, the gases can be ignited at a later stage, causing a pressure build-up due to the expansion of the heated combusted gas.

The probability of a single Li-ion cell failure, “field failure”, based on the number of produced cells compared to the number of reported fire failures, is typically about 1 ppm (1 cell failure in 1 million cells) [14, 15, 16]. However, the statistics are not well reported. For a large battery pack, the mathematical probability of a single cell failure to occur within that pack will increase, simply because of the large number of cells. Today there are no commercially intrinsically safe Li-ion battery cells, so cell failures will continue to happen. Furthermore, the Battery Management System (BMS) protects the cells, but it cannot protect the battery from all possible scenarios. Additionally, the BMS and its sensors can fail. External factors, such as external heat or mechanical impact, can lead to battery failures. Since incidents will happen, it is important to focus on mitigating the consequences of a single or multiple cell failure by proper battery system design and counteractions, to hinder or delay cell-to-cell propagation [17, 18, 19]. Cell-to-cell propagation and module-to-module propagation can be minimized through battery design, e.g. by dividing the battery system into multiple compartments/modules or by

cell/module separation [20]. Potential active and passive cooling systems will also affect the risk for fire propagations, as well as the integration of the battery system within the vessel.

What makes the fire hazard with Li-ion batteries different compared to many other fire hazards is that all the prerequisites needed for fire are available inside the battery; the fuel, the heat or spark, and to some extent the oxygen. The oxygen is typically released from cell internal reactions involving the electrode materials. In addition, heat is produced during thermal runaway and when approaching thermal runaway, it is therefore important with cooling.

In order to prevent propagation of a thermal runaway or fire in a battery pack or module, it is essential to extinguish the fire but also to cool the cells sufficiently. However, it is typically difficult to stop and cool down a thermal runaway cell due to limited access to cool the cell surface in a battery pack or module, since cells are in many cases densely packed and surrounded by many other things in the battery pack.

Water is among the most cooling (per weight) capable extinguishing agents available and water or water-based agents can be used for the extinguishment of Li-ion battery fires. Care should, however, be taken when Lithium metal batteries are on fire, as water on burning metal could result in formation of hydrogen. This fact has in some cases resulted in recommendations that water should not be used for Li-ion batteries, and instead that extinguishing agents for metal fires should be used.

Some advice on extinguishment of fire in Li-ion batteries can be found on for example YouTube or in commercial ads. However, in many cases there is very little data available to support such advice. Videos on YouTube can for example show one specific case where the extinguishing agent is distributed towards a fully exposed battery cell. There is often no comparison data without the use of any agent, so it could very well be that the agent is applied when the cell self-extinguishes due lack of fuel in the cell. There is also usually no information on how the agent would behave when the cell is inside a battery module or pack.

Furthermore, in many information sources it is unclear if the batteries discussed are Li-ion or lithium metal type. Both battery types are commonly referred to as “Lithium batteries” when it comes to e.g. transport regulations, but they are fundamentally different when it comes to many aspects, including fire extinguishment.

Other advices have stated that extinguishing agents should not be distributed inside battery modules. This advice probably originates from cases where cutting tools have been used for injecting the agent. However, as supporting data is lacking, it is difficult to determine the validity of this instruction.

A recent study [1] identified that there is a lack of test methods for fire-fighting systems to be used for energy storage battery systems. The same study also identified several contradicting recommendations on appropriate extinguishing agents for battery fires on board ships and an uncertainty on what type of fire extinguishing systems that are suitable.

A recent study with relevance for the project was performed by DNV-GL, who conducted a test series with different extinguishing agents and different Li-ion cells [21]. The series was conducted in order to provide answers to some specific questions from fire and

rescue services, in particular related to gas emissions. The results are reported as answers to these questions, which means that some aspects and data are missing in the report, such as how the agent was applied etc. The objective of the tests was directed towards energy storage battery systems installed in buildings, but it does not address extinguishing systems installed in the battery packs, only external fire-fighting.

This project provides results from tests using different extinguishing agents and application methods against fire in Li-ion cells mounted in a purpose-built module mock-up. The objective of the project was to indicate suitable extinguishing agents and application methods, but no specific design recommendations were sought. The module was designed to mimic the limited accessibility towards the cell, both in case of external and internal application of the agent.

3 Battery fire test set-up

In order to test both total compartment application (with water spray and water mist) and direct agent injection into the module, the test set-up comprised a test compartment mimicking a possible battery room and a purpose-built box mimicking a battery module.

To compare different agents and application methods, only one batch of battery cells was used in all tests. The cells used were chosen based on availability to the project and suitability. The fire initiation and test procedure were designed to make the fire test scenario as repeatable as possible. Fire development in Li-ion batteries and cells is, however, in general not very repeatable.

3.1 Battery cell

The Li-ion cell used for the tests was chosen based on availability to the project and suitability for the tests. The cells were commercially available and produced by Enertech International around 2009. The cells were of pouch type and high quality “automotive-classed” cells. The nominal capacity of the cells was 20 Ah and they had a carbon anode, a lithium iron-phosphate (LFP), LiFePO_4 , cathode and an organic electrolyte. The cells were all from the same batch.

The usage history of the tested cells is unconfirmed. From production around 2009, the cells were stored unused until used in this project in 2017. Consequently, the cells in this project were about eight years old, i.e. they had a calendar life of about eight years. This is a significant time in relation to the expected life time. This study therefore studied aged cells, in contrast to many other studies where fresh and new battery cells are typically tested [22].

In order to verify the status of the cells, each cell was evaluated individually. The cell weight and the open current voltage (OCV) were first measured. Then the cells were fully charged and discharged completely one time to obtain their capacity. After the discharge, each cell was fully charged again and then discharged 10% to set the cell at 90% state of charge (SOC). Furthermore, the OCV was measured a second time after one week from the capacity test.

In total, 100 cells were verified. Two of the cells showed potential small anomalies and were therefore discarded while the remaining cells were used in the fire extinguishing tests. Table 1 shows results from the evaluation tests. The measurements showed that an average of 19.7 Ah was still available in the cells, compared to the nominal 20 Ah. Consequently, no significant loss of capacity had occurred despite the eight-year calendar ageing.

Table 1 Results from verification of cell status based on data from 98 measured cells

| Parameter | Average value (standard deviation) |
|--------------------|------------------------------------|
| Cell weight | 660.4 g (2.4 g) |
| Capacity* | 19.70 Ah (0.29 Wh) |
| OCV after one week | 3.31 V (0.0023 V) |

* Charging using constant current (CC), then constant voltage (CV) and charging between 2.5 V and 3.65 V with 5 A (corresponding to a C/4 current) and 1 A cut-off current. Discharging between 3.65 V to 2.5 V with 5 A. The capacity value presented in the table is the C/4-discharge-capacity.

3.2 Thermal runaway initiation

For thermal runaway/fire initiation it was chosen to heat the cell from underneath using an electric heating element. The heating of the cells proved to be repeatable using this method. As the cells used for the test typically do not ignite from an external heat source only, and in order to ensure a repeatable fire scenario, a small propane gas flame was used as a pilot flame, igniting the combustion gases released from the cell during heat-up.

Another initiation method for thermal runaway that is often used is overcharge. Overcharge does typically result in a more vigorous and rapid fire. Even though such a fire might better represent a fire due to e.g. an internal short circuit, it is difficult to use it to compare different extinguishing agents and application methods as the fire develops very fast. The heating initiation method was chosen to provide a repeatable fire that was slow enough to allow comparison between different agents and application methods.

The idea of using several cells in each test was also abandoned as pre-tests showed this to be not particularly repeatable in temperature development, since it depends on how the cells swell and come in contact with each other. Instead it was decided to use a plate thermometer to indicate the heat exposure towards neighboring cells.

3.3 Simulated battery module

In order to mimic a battery module, the battery cell was positioned inside a cubic box. The box was fabricated from nominally 2 mm thick metal sheets with a frame size of 400 mm by 400 mm by 400 mm (height). One side consisted of a fire rated glass window to facilitate visual observations and video recording. As a lid, a metal sheet was used. The lid was placed to provide a small opening around the perimeter of the box of 20 mm, in order to avoid pressure build-up and potential severe consequences during tests (module rupture due to explosion). The lid was larger than the box (100 mm in all directions) in order to limit direct application of extinguishing agents from the outside.

The box was positioned on a table sized 800 mm by 800 mm with its top 680 mm above floor. The table top was built from a perforated steel plate which prevented water from accumulating.

The battery cell was placed directly on an electric heating element that heated the cell from underneath. Three non-combustible boards with 10 mm thickness were placed under the heating element (between the element and the table). Thermal insulation was also used and placed between the non-combustible boards. A pilot flame propane gas

nozzle was fixed above the test object. The battery cell, the heating element and the pilot flame nozzle were mounted inside the box.

Four perforated steel sheets were fixed inside the box above the battery cell to mimic that battery modules are densely packed which make the access of extinguishing agent to individual cells difficult. A dummy cell, consisting of a Plate Thermometer (see the description in Section 4), was used to evaluate the degree of fire control in the tests. It was placed above the battery cell. The vertical distance from the top of the battery cell to the Plate Thermometer was about 1 and a half cm at the initiation of the test. However, this vertical distance decreased during testing as the cell swelled from heating. The simulated battery module is shown in Figures 1 and 2.

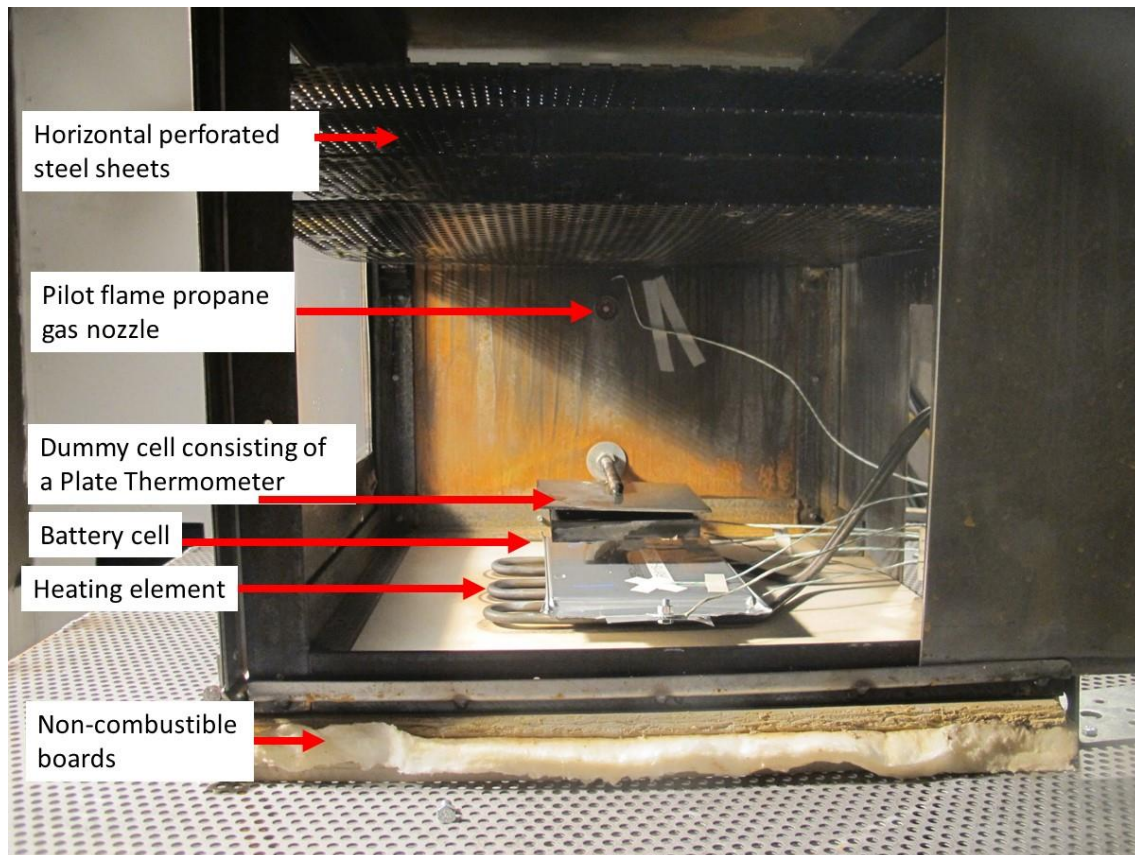


Figure 1 The simulated battery module.



Figure 2 The simulated battery module was fabricated from metal sheets with a frame size of 400 mm by 400 mm by 400 mm (height). One side consists of a fire rated glass window to facilitate visual observations and video recordings.

3.4 Fire test compartment

A test compartment was built to simulate a possible battery room. The floor area of the compartment was 3.66 m by 3.66 m (13.4 m²) and the ceiling height 2.5 m. The compartment was built from non-combustible wall boards, with a nominal thickness of 12 mm, on a framework of wood studs and with a doorway opening with a door. The test compartment was sealed closed during all tests. The walls of the compartment were equipped with two window openings to facilitate visual observations and video recordings. One window provided an overview of the set-up and one window was facing the window of the simulated battery module. One video camera was placed at each window. Two spotlights were also installed inside the compartment. The compartment is shown in Figure 3. The table with the simulated battery module was positioned in one of the quadrants of the test compartment, as seen in Figure 4.



Figure 3 The fire test compartment used in the tests. The compartment was sized 3.66 m by 3.66 m and had a regular doorway opening at one of the walls. The video camera providing a room overview is seen to the right.



Figure 4 The simulated battery module was positioned on a table inside the test compartment.

4 Instrumentation and measurements

The following measurements, instrumentation and documentation of the tests were provided:

Surface temperature of the battery cell

A total of four 0.25 mm wire thermocouples were taped (3M glass fiber tape) on the surface of the cell; two thermocouples on its top surface and two on its bottom surface.

Heat exposure from the battery cell

A Plate Thermometer device was installed above the battery cell. The Plate Thermometer consists of a 100 mm by 100 mm steel plate, nominally 0.7 mm thick. A sheathed 1 mm diameter thermocouple is spot-welded to the backside of the steel plate and the backside is insulated with 10 mm thermal insulation. The intent was to assess the heat exposure to an adjacent battery cell. The device is sensitive to both heat convection and heat radiation, whereas a conventional thermocouple mainly captures heat convection (gas temperature). In this test series, heat would be transferred also by conduction as the cell came into contact with the plate thermometer when it swelled. By measuring the temperature of the steel plate, the data could indicate whether fire would spread to the “adjacent battery cell”, although no specific temperature threshold was used to determine this in this project.

Voltage of the cell

Voltage measurement was made by making a hole in the tabs of the cell, made using a simple A4 copy paper perforator. M4 bolts were used to attach the cable made of T/C wire. The voltage of the cell, together with visible flames, determined the time when the fire-fighting system should be manually activated.

Gas temperatures inside the test compartment

Thermocouples were installed 10 mm, 100 mm, 200 mm, 300 mm, 400 mm, 500 mm, 1000 mm, 1250 mm (mid-height) and 1500 mm, respectively, below the ceiling of the room. The thermocouple tree was positioned 915 mm by 915 mm from one of the corner walls. Welded Type K thermocouple wire with a diameter of 0.25 mm was used.

Concentration of Oxygen (O₂)

For the nitrogen gas fire-extinguishing system tests, one oxygen concentration sampling point was installed inside the simulated battery module.

Water flow rate

A Krohne 0-200 liter/min flow meter was used for the total compartment system tests.

System operating pressure

For the water spray and water mist system tests, a pressure transducer was installed close to the nozzle in order to document the system operating pressure.

Video recordings

One video camera was positioned in front of the window opening of the simulated battery module. Another video camera provided an overview of the test set-up inside the test compartment. Two spotlights were used inside the compartment to get sufficient lighting.

5 Fire scenario

Before the actual test series, tests were conducted in order to establish a test procedure facilitating repeatable tests and providing benchmark test data for the extinguishing tests. For the fire initiation, an electrical heating element (a charcoal barbeque lighter) was used, placed underneath the battery cell. As the released gases from a ruptured battery cell do not always ignite by themselves, it was decided to use a pilot flame.

Based on pre-tests it was decided to use the following procedure:

- The measurements, pilot flame and heating element were started at about the same time. The video cameras were started one minute later.
- The application of agent (where applicable) was initiated when a fire had started, based on visual observation and a reduction of the measured voltage of the battery cells to below 2 V.
- The propane gas for the pilot flame was stopped when application of the extinguishing agent was initiated (where applicable) or after fire ignition (applicable for the free-burn tests). The electrical heating element was turned off 2 minutes after initiated application of extinguishing agent. The electrical heating element was left on to distinguish between temperature development due to the extinguishing system and due to the electrical heating element being turned off.

Free-burn tests were run following to provide a benchmark for the extinguishing tests. Figure 5 shows the temperature readings of the Plate Thermometer and the voltage readings during the three free-burn tests, conducted according to the test procedure that was later used in the test series. As can be seen, Tests 2 and 3 show a very similar temperature increase while the temperature increases a bit earlier in Test 4. This is in line with the observation that the voltage drop occurs earlier in Test 4.

Figure 6 shows the temperature readings, the voltage and when the heating element was turned off in Test 2. The temperature reading at the bottom surface of the cell increases slowly in the beginning and then starts to increase more rapidly after about 5 minutes. It is important to be aware that the temperature at the bottom surface of the cell will be influenced by how close the tip of the thermocouple is to the electric heating element. Hence, those readings were not evaluated in detail but rather included as an indication of when heating was initiated.

The temperature at the top surface of the cell increases slower until the voltage drop, after which TC1 increases rapidly. This is when hot gases are released from the cell and ignited. This temperature later drops when all the gases have been released and consumed in the fire.

For TC2, it can be observed that the temperature increases, but when the cell swells due to heating the thermocouple gets in contact with the Plate Thermometer and these two temperatures align.

At about 14 minutes, the electric heating element was turned off, which results in a drop in the temperature of TC3 and TC4 at the bottom surface of the cell, while the Plate Thermometer and TC2 temperature continue to increase for a while. As the electric heating element has an immediate effect on the results, it was decided to leave it on for

another 2 minutes after the extinguishing system was activated. Thereby it could be possible to distinguish between a temperature drop caused by the extinguishing system and a temperature drop due to turning off the electric heating element.

Similar trends were observed in all of the three free-burn tests, but the timing and the temperature levels at which the different events occurred varied to some degree. It is therefore important that the extinguishing tests are evaluated considering the temperature evolution when the extinguishing system is activated.

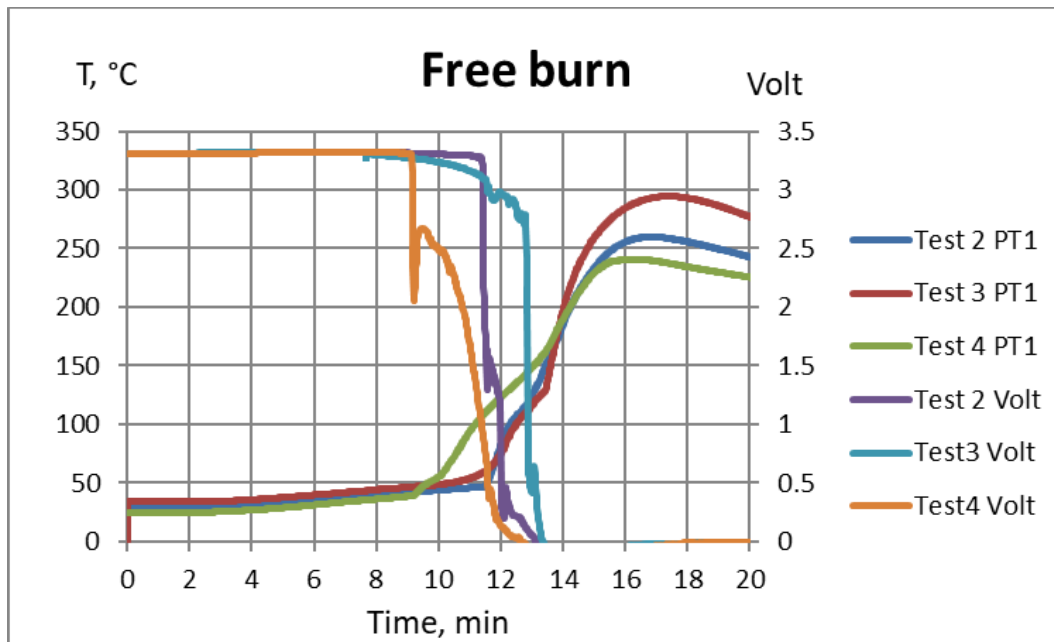


Figure 5. Temperature readings of Plate Thermometer and voltage readings in three free-burn tests.

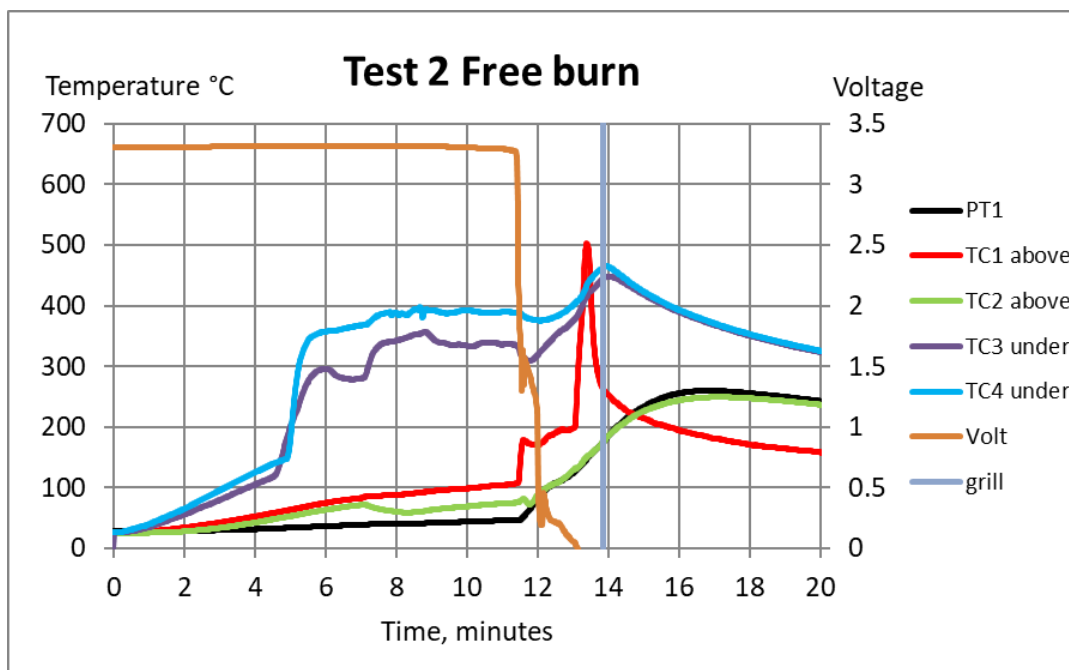


Figure 6. Temperature readings, voltage drop and the electric heating element turn-off in the free-burn test in Test 2.

6 Fire-extinguishing systems

Fixed water spray and water mist systems are commonly used as total compartment application systems, i.e. providing complete protection of a compartment by simultaneous operation of all nozzles in the space. In this series of tests, total compartment water spray and water mist systems were used. Fire tests were also conducted where the agent was directly injected into the battery module. The following application methods and agents were used:

- **Total compartment system fire tests**, where the system nozzle was positioned at the ceiling of the test compartment:
 - Water spray system tests.
 - Low-pressure water mist system tests.
 - High-pressure water mist system tests.
- **Direct injection fire tests**, distributing the agent directly into the battery module:
 - Water (only) spray nozzle tests.
 - Water spray nozzle tests with a 0.5% admixture of a Class A foam agent.
 - Water spray nozzle tests with a Class F foam agent. Note: Pre-mix solution.
 - Tests with Compressed Air Foam System (CAFS), using a portable extinguisher.
 - Nitrogen gas system tests.
 - Test with Aqueous Vermiculite Dispersion (AVD), using a portable extinguisher.

The fixed water spray and water mist compartment application systems were selected to represent the different recommendations given by classification societies for the protection of battery rooms. The agents that were directly injected into the module were either recommended for this particular battery application or that were judged to be of interest to investigate.

6.1 Total compartment system tests

Three different total compartment systems were tested: one water spray system, one low-pressure water mist system and one high-pressure water mist system.

6.1.1 Water spray system

A medium velocity water spray nozzle was used to represent a traditional water spray system. The nozzle was an open (non-automatic), pendent directional discharge water spray nozzle with an external deflector that discharged a uniformly filled cone of medium velocity water droplets. The nozzle used in the tests had no nozzle strainer. Figure 7 shows the nozzle used.



Figure 7 The pendent open (non-automatic) medium velocity water spray nozzle used in the total compartment system tests.

The nozzle had a 180° spray angle to cover the floor area of the test compartment. The desired discharge density of 5 mm/min corresponded to a nominal water flow rate of 67.0 liter/min. The chosen K-factor of 43.2 (liter/minute)/bar^{1/2} resulted in a nominal required operating pressure of 2.4 bar. The nozzle had a minimum orifice diameter of 8.33 mm.

The nozzle was installed with the frame arms parallel with the walls of the test compartment, at the center point of the ceiling of the test compartment.

6.1.2 Low-pressure water mist system

A commercial, pendent low-pressure single-orifice water mist nozzle was used to represent a low-pressure water mist system. The nozzle is intended for use with total compartment water mist deluge systems. It is an intermediate pressure nozzle which utilizes a single fluid jet impinging on a diffuser to produce a spray having a range of water droplet sizes suitable for the extinguishment of Class B fires, as well as incidental Class A fires. The nozzle had a K-factor of 3.5 (liter/minute)/bar^{1/2}. The nominal flow rate of 13.6 liter/minute at the recommended minimum operating pressure of 15 bar provided a discharge density of 1.0 mm/min over the floor area of the test compartment, i.e. one-fifth the water density of the tested medium velocity nozzle. Figure 8 shows the nozzle used.



Figure 8 The pendent open (non-automatic) low-pressure single-orifice water mist nozzle used in the total compartment system tests.

The nozzle was installed with the frame arms parallel with the walls of the test compartment, at the center point of the ceiling of the test compartment.

6.1.3 High-pressure water mist system

A commercial, pendent high-pressure water mist nozzle was used to represent a high-pressure water mist system. The nozzle is an open (non-automatic) multi-orifice nozzles without any external deflector. The nozzle is intended for use with total compartment, engineered, water mist deluge systems. When spraying, the nozzle discharge forms a solid cone-shaped spray pattern of high velocity jets that breaks up into small water droplets a relatively short distance from the nozzle orifices. The overall spray angle is approximately 160°. The nozzle had a K-factor of 3.5 (liter/minute)/bar^{1/2}.

The nominal flow rate of 24.7 liter/minute at the recommended minimum operating pressure of 50 bar provided a discharge density of 1.8 mm/min over the floor area of the test compartment, i.e. almost twice the water density of the tested low-pressure single-orifice water mist nozzle. Figure 9 shows the nozzle used.

The nozzle was installed at the center point of the ceiling of the test compartment.



Figure 9 The open (non-automatic) high-pressure water mist nozzle used in the total compartment system tests.

6.1.4 Summary of total compartment system test parameters

The system test parameters described above are summarized in Table 2. Two tests were conducted with the water spray system and the low-pressure and high-pressure water mist system, respectively.

Table 2 The system test parameters for the total compartment system tests.

| Test | System | Nozzle K-factor (metric) | Measured water flow rate (liter/min) | Corresponding water pressure (bar) | Calculated density (mm/min) over the floor |
|------|--------------------------|--------------------------|--------------------------------------|------------------------------------|--|
| 17 | Water spray | 43.2 | 68 | 2.5 | 5.1 |
| 18 | Water spray | 43.2 | 69.9 | 2.6 | 5.2 |
| 19 | Low-pressure water mist | 3.5 | 13.6 | 15 | 1.0 |
| 21 | Low-pressure water mist | 3.5 | 13.6 | 15 | 1.0 |
| 22 | High-pressure water mist | 3.5 | 25.0 | 51 | 1.9 |
| 24 | High-pressure water mist | 3.5 | 24.6 | 49 | 1.8 |

6.2 Direct injection tests

Four different types tests were conducted with water only, three different foams, a gaseous agent (nitrogen) and an agent developed for Li-ion batteries.

6.2.1 Full cone water spray nozzle tests

For the full cone water spray nozzle tests, a single water spray nozzle was installed at the top of the simulated battery module. Full cone nozzles with axial-flow, single-orifice, and a spray angle of 90° were used. Two nozzles with different K-factors were tested. These types of nozzles provide a uniform water distribution over the whole circular impact area.

The four layers of perforated horizontal steel sheet plates inside the simulated battery module acted as an obstruction for the water spray. The spray angle of the nozzles was chosen such that complete coverage of the horizontal surface area of the top steel plate was achieved. Figure 10 shows the position of the water spray nozzle relative to the four perforated steel sheet plates inside the simulated battery module. The vertical distance, measured from the tip of the nozzle to the topmost steel plate, was approximately 100 mm.

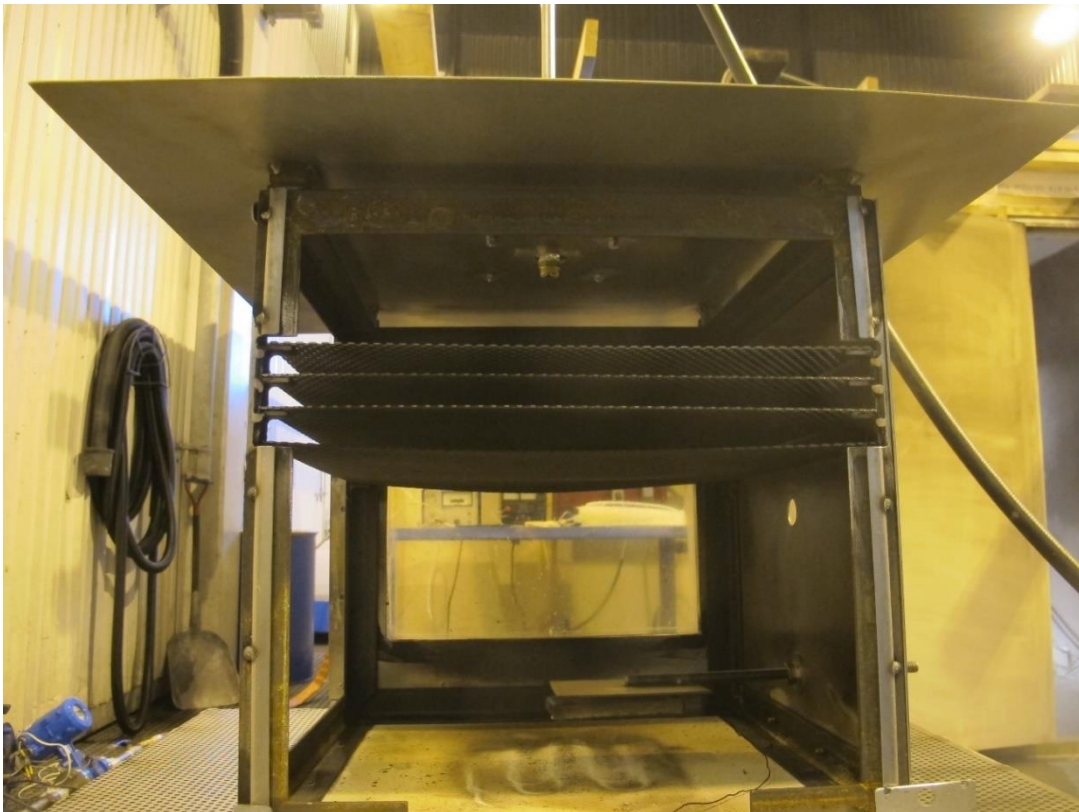


Figure 10 Position of the full cone water spray nozzle relative to the four horizontal perforated steel sheet plates, depicted from the backside of the simulated battery module, with the back wall removed.

Two different nozzles were used, one with a K-factor of $5.38 \text{ (liter/minute)/bar}^{1/2}$ and another with a K-factor of $3.52 \text{ (liter/minute)/bar}^{1/2}$. The larger of the nozzles provided a flow rate of 7.1 liter/minute at approximately 2 bar and the smaller nozzle a flow rate

of 5.0 liter/minute at the same pressure. Figure 11 shows the water distribution inside the simulated battery module at these water flow rates.



Figure 11 Distribution of water inside the simulated battery module when discharging 5.0 liter/minute (left) and 7.1 liter/minute (right), depicted from the backside of the simulated battery module, with the back wall removed.

6.2.2 Class A foam tests

Tests were conducted with the water spray nozzle discharging nominally 5.0 liter/minute using a Class A foam agent to document any improved performance compared to pure water.

Class A foams (also known as “wild fire foam” and “wetting agent”) are intended for use against Class A fires, such as wood, paper, textiles or rubber. They contain a blend of surfactants that enable strong wetting and foaming properties and are often intended for use at a low concentration of between 0.1% and 1%. The type of foam offers improved extinguishment of Class A fires by providing deep penetration of the water into the burning material. At low concentrations it is also highly effective as a wetting agent. It can be used with both aspirating and non-aspirating discharge devices. For the current tests, a concentration of 0.5% was used and water and the foam agent were pre-mixed in a pressure vessel.

According to the manufacturer, the Class A foam agent that was used is a non-hazardous, biodegradable substance, totally free from fluorinated surfactants.

6.2.3 Class F foam tests

Tests were conducted with the water spray nozzle discharging nominally 5.0 liter/minute using a Class F foam agent to document any improved performance compared to pure water.

The Class F agent used was an aqueous solution of high activity salts and stabilizers for use on oil, fat and grease related fires as found in restaurant appliances such as deep fat fryers, griddles, chip pan hoods and ventilating equipment. The agent was a pre-mix, which eliminated the need for dilution before charging the system.

According to the manufacturer, the Class F agent that was used is formulated using raw materials specially selected for their fire performance and their environmental profile and the foam is biodegradable.

6.2.4 CAFS tests

A Compressed Air Foam System (CAFS) uses a solution of water and a Class A foam concentrate in a mixture with compressed air to generate a high-quality foam. Originally, compressed air foam was used in wildland fire fighting, but has since been adapted for fire-fighting in structural fires.

For these tests, a portable CAFS unit was used and the nozzle was connected directly to the top of the simulated battery module. The unit consisted of a 10.4 liter water cylinder and a 2 liter pressure cylinder with compressed air at 300 bar.

Two foam qualities were possible to select by pushing a simple bolt on the unit, a “wet” or a “dry” foam. According to the manufacturer, the water flow rate is 5.4 liter/minute and the discharge time approximately 115 seconds for the “wet” foam and 11 liter/minute over 55 seconds for the “dry” foam. The working pressure was nominally approximately 8 bar.

For the first test, the air-to-solution ratio was regulated to generate a “wet” foam, i.e. the water in the foam would drain more quickly in the presence of heat. On the other hand, the foam would more likely flow around obstructions. For the two additional tests, the foam air-to-solution ratio was regulated to generate a “dry” foam, i.e. the water in the foam would drain less quickly in the presence of heat but it is more rigid.

6.2.5 Nitrogen gas tests

Nitrogen is an inert gas that extinguishes fire by oxygen depletion. It has a density nearly equivalent to air, which results in lower loss of agent from an enclosed compartment during and following discharge as compared to heavier gases. The gas is colorless, odorless and electrically non-conductive. Gaseous agents are recognized as effective for the extinguishment of flammable liquid fires, fires in electrical equipment as well as ordinary Class A fires. However, there may be hazards where gaseous agents are not suitable or certain circumstances or situations that require special precautions.

It was not possible to obtain any commercial nitrogen gas system that was designed for the fire hazard represented in the tests. Instead, a regular nitrogen gas container was used. The nitrogen was regulated down to a normal pressure and a flow of about 160 NL/min, introduced directly into the simulated battery module with a coarse hose. The nitrogen concentration was measured in the box and showed that the nitrogen did not reach the bottom of the box with this low momentum flow without any nozzle if the gas was introduced in the lid. As a very low momentum flow is usually not used for gaseous agents, it was decided to introduce the nitrogen close to the bottom. Figure 12 shows the connection of the gas hose line to the top of the simulated battery module. This approach was used only for the first test. Figure 13 shows the approach for the tests thereafter, where the connection point was moved to the side of the simulated battery module.



Figure 12 The connection of the nitrogen gas hose line to the top of the simulated battery module.

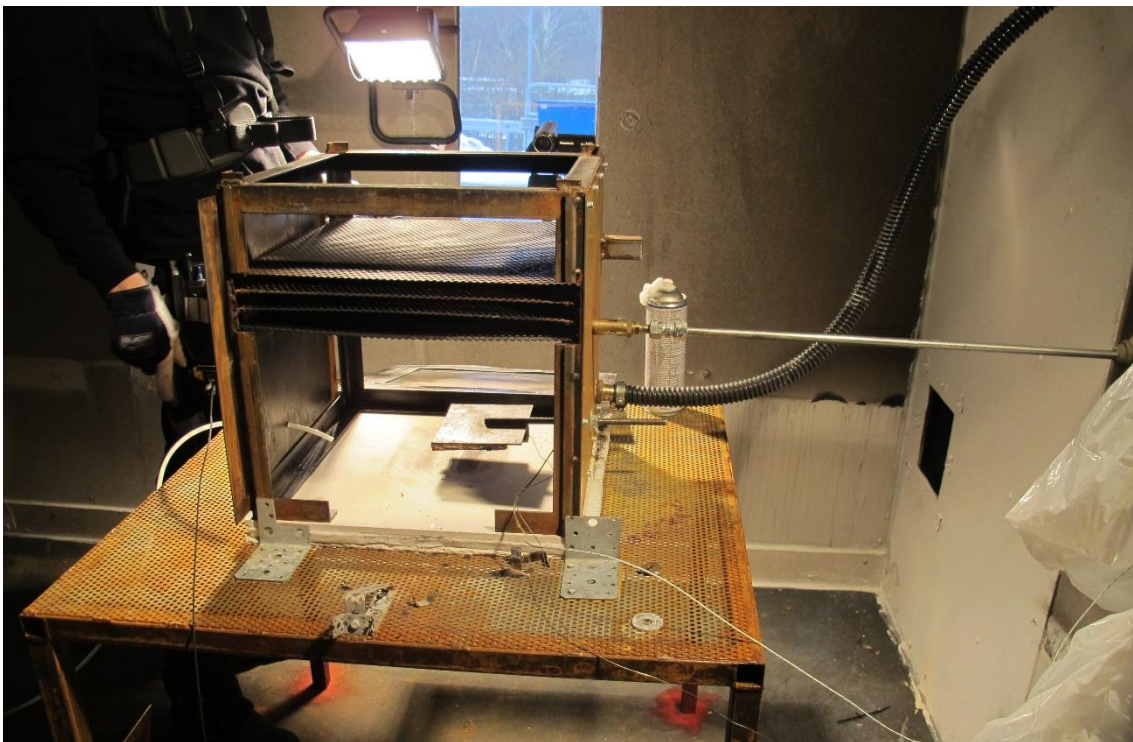


Figure 13 The connection of the nitrogen gas hose line to the side of the simulated battery module, as seen from the back side. With this approach the gas was not required to pass through the perforated steel sheet plates at the top of the module.

6.2.6 Aqueous Vermiculite Dispersion (AVD) test

The Aqueous Vermiculite Dispersion (AVD) consisted of vermiculite platelets dispersed in water. Vermiculite is the name given to a group of hydrated laminar aluminum-iron-magnesium silicates. It undergoes significant expansion when heated.

According to the manufacturer, AVD is non-flammable and has excellent thermal insulation properties. It has a solid content of 13.5% and a Brookfield viscosity [Sp3, 100 rpm] of <500 cP. The color of the product is gold/brown. When applied, AVD creates a film over the top of the fire. The film instantly dries to produce a non-flammable oxygen barrier.

For this test, the AVD agent was contained in a portable fire extinguisher with a cylinder volume of 6 liters, filled with 4.8 liters of the agent at 14 bar pressure. The nozzle of the fire extinguisher was connected to the top of the simulated battery module. According to the manufacturers, the nozzle is designed to create a mist for application directly onto a battery. Figure 14 shows the arrangement.

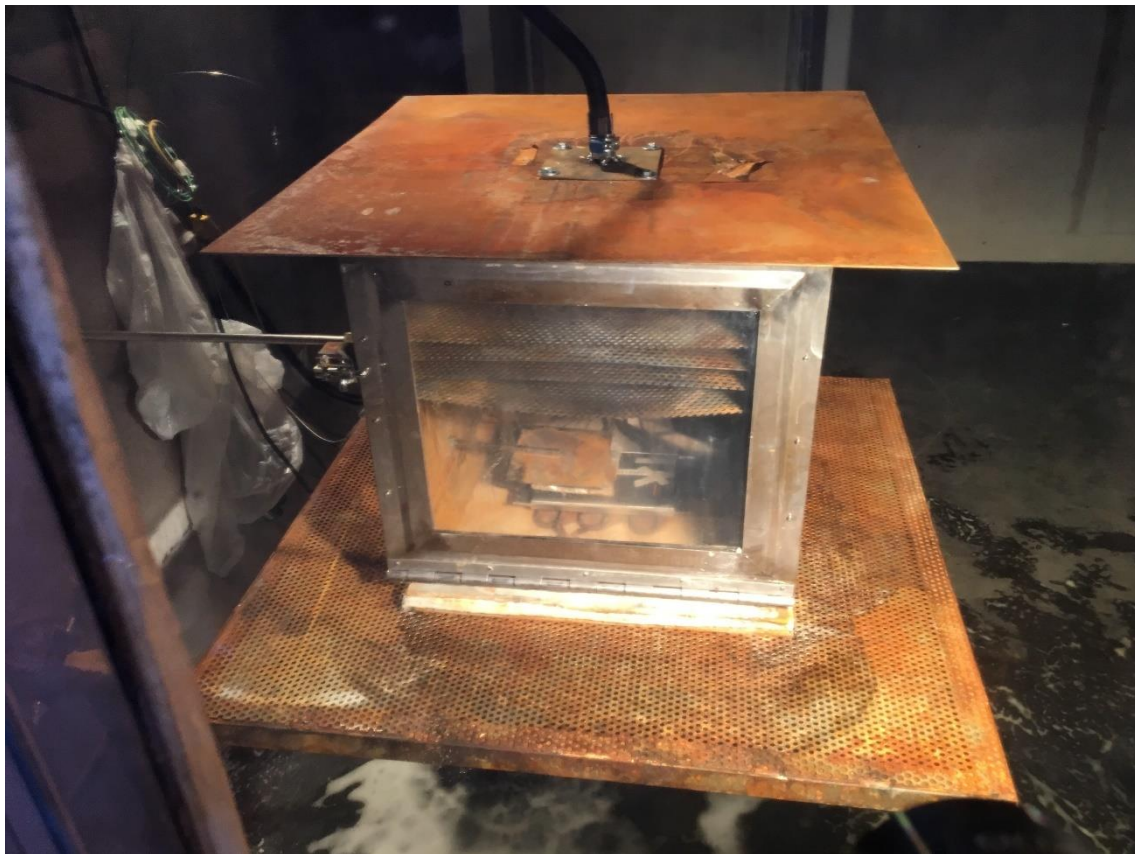


Figure 14 The connection of the hose line for the AVD agent to the top of the simulated battery module.

The AVD agent was distributed for approximately 2 minutes, until the cylinder was empty. Based on the amount of agent in the cylinder, the mean flow rate was around 2.4 liter/minute.

6.2.7 Summary of direct injection test parameters

The system test parameters described above are summarized in Table 3. Most of the main tests were repeated.

Table 3 The system test parameters for direct injection system tests.

| Test | System | Nozzle K-factor (metric) | Measured flow rate (liter/min) | Corresponding pressure (bar) | Comments |
|------|----------------------------------|--------------------------|--------------------------------|------------------------------|--------------------------------------|
| 7 | Full cone nozzle with water only | 5.38 | 7.1 | 1.75 | |
| 8 | Full cone nozzle with water only | 5.38 | 7.1 | 1.75 | Repeat of Test 7 |
| 9 | Full cone nozzle with water only | 3.52 | 5.0 | 2.0 | |
| 10 | Full cone nozzle with water only | 3.52 | 5.0 | 2.0 | Repeat of Test 9 |
| 13 | Class A foam | 3.52 | 4.5 | 1.6 | |
| 14 | Class A foam | 3.52 | 5.2 | 2.2 | Repeat of Test 13 |
| 15 | Class F foam | 3.52 | 4.6 | 1.7 | |
| 16 | Class F foam | 3.52 | 5.0 | 2.0 | Repeat of Test 15 |
| 30 | Nitrogen gas system tests | | | | Connection to the side of the module |
| 31 | | | | | Repeat of Test 30 |
| 35 | CAFS | - | ≈ 11.0 | 8 | Wet foam |
| 36 | CAFS | - | ≈ 5.4 | 8 | Dry foam |
| 37 | CAFS | - | ≈ 5.4 | 8 | Dry foam. Repeat of Test 36. |
| 39 | AVD | - | ≈ 2.4 | 14 | One test only |

Note: Figures for CAFS and AVD are based on manufacturers' specifications, not measurements.

7 Results

The results from the tests are presented in Appendix A.

The performance of the tested agents was evaluated based on the temperature evolution of the Plate Thermometer in comparison with the temperature obtained in three free-burn tests and to some extent visual observations. Table 4 shows the peak temperatures measured with the Plate Thermometer during the free-burn fire tests, respectively, and the calculated mean peak temperature based on these tests. The peak temperatures were relatively consistent, except for Test 3 where the peak temperature was slightly higher.

Table 4 Peak temperatures measured with the Plate Thermometer during three free-burn fire tests along with the calculated mean temperature.

| Test | System | Peak temp. (°C) of Plate Thermometer | Mean temp. (°C) of Plate Thermometer |
|------|-----------|--------------------------------------|--------------------------------------|
| 2 | Free-burn | 260 | 265 |
| 3 | Free-burn | 295 | |
| 4 | Free-burn | 241 | |

7.1 Total compartment system test results

Table 5 shows the temperatures measured with the Plate Thermometer at the manual activation, the peak temperature and the mean peak temperature, respectively, for all the total compartment system tests. All the total compartment tests showed similar results, i.e. there was no apparent influence on the temperature measurement points. Instead, the temperature continued to rise despite the activation of the systems.

Table 5 Key temperatures measured with the Plate Thermometer during the total compartment system tests.

| Test | System | Temp. (°C) of Plate Thermometer at activation | Peak temp. (°C) of Plate Thermometer | Fire extinguished? | Temp. increase (°C) after activation | Influencing temperature development |
|------|--------------------|---|--------------------------------------|--------------------|--------------------------------------|-------------------------------------|
| 17 | Water spray | 111 | 221 | No | 110 | No |
| 18 | Water spray | 100 | 218 | No | 118 | No |
| 19 | Low-pressure mist | 49 | 242 | No | 193 | No |
| 21 | Low-pressure mist | 161 | 272 | No | 111 | No |
| 22 | High-pressure mist | 124 | 264 | No | 140 | No |
| 24 | High-pressure mist | 101 | 248 | No | 147 | No |

It can be observed that the temperature at the manual activation of the systems in the compartment varied considerably between the tests. This is because of the variation of

cell swelling from test to test. The variation in peak temperature for each of the tests was, however, relatively small and the peak temperature is similar to the peak temperature achieved during the free-burn fire tests. The mean peak temperature for all three systems is relatively similar, indicating that the performance was similar and insignificant.

The mean peak temperature for the total compartment system tests was 244°C, which is comparable to the mean peak temperature obtained during the free-burn fire tests (265°C). This indicates that none of the systems had any actual effect on the severity of the fire in the battery cell. This was expected, due to the shielding associated with the position of the cell inside the simulated battery module. Fire extinguishment was not achieved in any of the total compartment system tests. The fire burnt out as the combustible material was consumed.

7.2 Direct injection test results

Table 6 shows the temperatures measured with the Plate Thermometer at the manual activation of direct injection system, the peak temperature and the mean peak temperature, respectively.

The water flow rate of 7.1 liter/minute reduced the peak temperature of the Plate Thermometer considerably as compared to the flow rate of 5.0 liter/min. However, the system was activated too early in Test 8 and the equipment was wet when Test 7 was started. This influenced the temperature of the Plate Thermometer before the activation of the system, the temperature increase after activation was about the same, independent of the water flow rate. The temperature variation between the repeated tests was small. For all tests with water only, the fire was extinguished more or less immediately.

The Class A and Class F foam tests were conducted using a nominal flow rate of 5.0 liter/min in order to determine any improved performance compared to pure water. The reduction in peak temperature of the Plate Thermometer was, however, marginal and no change in performance due to the specific foam agent was noticed. It should especially be considered that the temperature increase after activation was somewhat higher for the foam systems than for the water, but the peak temperature was lower in the foam system tests. The fires were almost immediately extinguished also in the foam system tests. It could therefore be argued that no performance improvements attributable to the foam agents were observed compared to use of plain water.

Table 6 Key temperatures measured with the Plate Thermometer during the direct injection tests with different agents.

| Test | System | Temp. (°C) of Plate Thermometer at activation | Peak temp. (°C) of Plate Thermometer | Fire extinguished? | Temp. increase (°C) after activation | Influencing temperature development after activation |
|------|---------------------------|---|--------------------------------------|--------------------|--------------------------------------|--|
| 7* | Water spray, 7.1 l/minute | 28 | 48 | Yes | 30 | Yes |
| 8** | Water spray, 7.1 l/minute | 43 | 52 | Yes | 9 | Yes |
| 9 | Water spray 5.0 l/minute | 79 | 100 | Yes | 21 | Yes |
| 10 | Water spray 5.0 l/minute | 98 | 103 | Yes | 5 | Yes |
| 13 | Class A foam | 68 | 99 | Yes | 31 | Yes |
| 14 | Class A foam | 63 | 85 | Yes | 22 | Yes |
| 15 | Class F foam | 51 | 86 | Yes | 35 | Yes |
| 16 | Class F foam | 66 | 98 | Yes | 32 | Yes |
| 26 | Nitrogen | 129 | 285 | No | 156 | No |
| 30 | Nitrogen | 95 | 247 | Yes | 152 | No |
| 31 | Nitrogen | 108 | 273 | Yes | 165 | No |
| 35 | CAFS (Wet) | 115 | 124 | Yes | 9 | Yes |
| 36 | CAFS (Dry) | 99 | 203 | No | 104 | No |
| 37 | CAFS (Dry) | 45 | 92 | Yes | 47 | Yes |
| 39 | AVD | 55 | 104 | Yes, but long time | 49 | Yes |

*) The low temperature of the Plate Thermometers was due to that the device and the box were already wet when the test started.

**) The nozzle was activated prior the drop in the voltage signal, and therefore earlier than in the other tests.

Figure 15 shows the oxygen concentration measured inside the simulated battery module during the nitrogen gas system tests. In Test 26, the nitrogen gas did not reach the cell due to the low momentum input at the top of the module and the reduction in oxygen concentration was marginal. It is likely that the gas escaped though the top gap around the perimeter of the module in the absence of a nitrogen nozzle. The connection of the nitrogen gas hose line was moved to the side of the simulated battery module for Tests 30 and 31, in order to evaluate how a nitrogen system would act if it was properly installed.

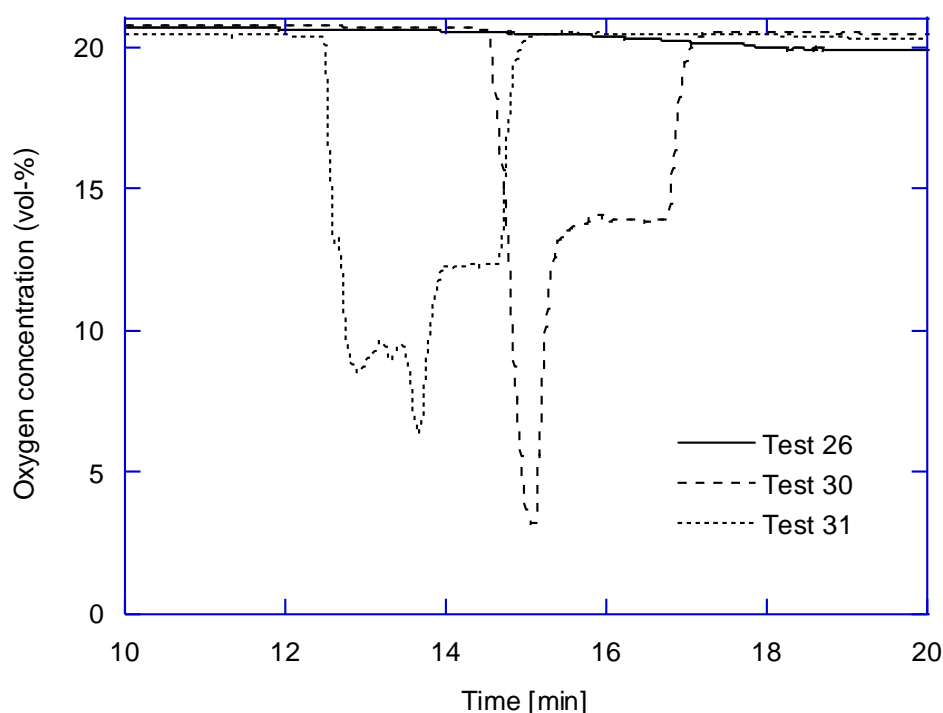


Figure 15 The oxygen concentration measured inside the simulated battery module during Tests 26, 30 and 31, respectively.

The minimum oxygen concentration inside the simulated battery module was 3.2 vol-% in Test 30 and 6.4 vol-% in Test 31. The oxygen concentration was below 10 vol-% for a little more than one minute in Test 30 and for approximately half a minute in Test 31, and below 15 vol-% for a bit more than two minutes in both tests.

The fires in Tests 30 and 31 were visually extinguished within 45-60 seconds after the activation of the inert gas system. The application of gas was stopped approximately one minute after fire extinguishment was determined and the rapid increase in oxygen concentration observed in the graphs occurred soon thereafter.

Cooling of the Plate Thermometer was limited from application of nitrogen as compared to the free-burn fire tests. For a practical application, this would call for a prolonged discharge or sequential discharges over a period of time that allow the fire and heated material to cool down. Additionally, the integrity of a battery module is an important parameter for maintaining a low oxygen concentration over a long time. As demonstrated by the tests, proper design of the system is also important to achieve distribution inside the battery module, allowing to reach all the cells.

For the first test with CAFS, Test 35, the air-to-solution ratio was regulated to generate a “wet” foam. The foam filled the entire simulated battery module with foam in approximately 20 seconds. This obscured the visibility in the module, but it is likely that the fire was extinguished within this time frame. The peak temperature of the Plate Thermometer was slightly higher than the temperatures obtained with the water spray nozzle when discharging 5.0 liter/min, while the temperature increase of the Plate Thermometer after activation was in the same order of magnitude as for the water spray nozzle.

For the second test with CAFS, Test 36, the air-to-solution ratio was regulated to generate a “dry” foam. The foam was not able to fill the module, probably because it was too light to overcome the overpressure generated by the fire. This resulted in a considerably higher peak temperature of the Plate Thermometer as compared to the temperature in Test 35. Visually it looked like the fire self-extinguished, since the foam did not reach the fire.

The third test, Test 37 was also conducted with a “dry” foam. The foam filled the entire simulated battery module with foam in approximately 20 seconds. This obscured the visibility in the module, but it is likely that the fire was extinguished within this time frame. Compared to Test 36, the fire seemed less severe and a smaller amount of smoke was generated. The peak temperature of the Plate Thermometer was slightly lower than the temperature recorded in Test 35.

Figures 17 through 19 show the fill-up of “wet” and “dry” foam, respectively, in the three CAFS tests. The observations during the CAFS tests indicate that the foam quality is essential to fill-up an obstructed volume and overcome any internal pressure generated by a fire.



Figure 16 The fill-up of “wet” CAFS foam inside the simulated battery module foam in Test 35.



Figure 17 The incomplete fill-up of “dry” CAFS foam inside the simulated battery module in Test 36.



Figure 18 The fill-up of “dry” CAFS foam inside the simulated battery module in Test 37.

The AVD agent was applied at the top of the simulated battery module but did not, due to its higher viscosity, penetrate the perforated horizontal steel sheet plates as fast as the other tested agents. Large amounts of the agent flowed to and over the sides of the bottommost steel plate and then across the bottom of the module and over the battery cell. The fire was fully extinguished once the cell was completely encapsulated. However, the AVD required a longer time to extinguishment compared to the other agents, and the temperature increase of the Plate Thermometer after activation was in the same order of magnitude as with the CAFS dry foam. Figure 20 shows a close-up photo of the spread of the AVD agent during the test, prior full fire extinguishment was achieved. In order to get AVD to more effectively pass through several sheets of perforated steel another nozzle and probably another viscosity would be required. Once the agent reached the burning cell it seemed effective to encapsulate a fire.



Figure 19 The spread of the AVD agent over the perforated horizontal steel sheet plates, prior full fire extinguishment.

8 Discussion

This report presents a limited study with the aim to provide publicly available test results from simple experiments, providing a basic understanding of Li-ion battery fire extinguishment. The objective was not to provide specific design recommendations for extinguishing systems but to evaluate the performance of different extinguishing agents and application methods. The tests were designed to demonstrate the performance differences of total compartment systems versus direct injection with water, foam, inert gas and an agent developed for Li-ion batteries.

The experimental set-up had limitations, in particular:

- The fire initiation method used was external heating of the cell combined with a small pilot flame. Heating is together with overcharge the predominant method of initiating thermal runaway for Li-ion cells. Overcharge can in many cases result in more vigorous fires. Such a violent fire could be more realistic and conservative, but it would make the comparison between the different tests much more difficult. It was therefore decided to use heating as the initiation method.
- The box mimicking the battery module or casing was to some extent open. Battery casings and modules can look very different, where some of them are more air-tight than others. The box was designed with gaps to be able to conduct the tests in a safe way and still mimic the difficulties for a total flooding agent to reach the cell. In addition, perforated steel sheet plates were used to mimic the dense material packaging in a module. It is essential to understand that one cannot base the design of a system on these tests, as they were arranged to demonstrate difficulties for agents and application methods.

Given these limitations it is still possible to observe that the tests indicate that fire extinguishment of a battery cell fire inside a battery module is unlikely when using total compartment water spray or water mist fire protection systems. The water droplets are simply not able to get inside the battery module and reach to the seat of the fire. Although no other fire protection systems were tested in the total compartment system tests, it is likely that only a gaseous agent would be able to reach to the seat of a fire inside a battery module.

A fire extinguishing agent will more likely have an effect if it is distributed inside the battery module. Several different fire extinguishing agents were evaluated direct injection into the battery module: plain water applied with a full cone water spray nozzle, Class A and Class F foams applied with the same nozzle, nitrogen gas, CAFS, and an agent (AVD) specifically developed for Li-ion battery fires, applied with the full cone water spray nozzle.

Pure water proved to be effective when sprayed from the top of the simulated battery module. The water penetrated the obstructions in terms of four horizontal layers of perforated steel sheet plates and the fire was promptly extinguished. The application of water did also provide cooling of the Plate Thermometer device that was used to simulate an adjacent battery cell. In a practical application, the integrity of the battery module is important if water is the intended fire extinguishing agent. Water would need to be

applied at, or at least close to, the top of the battery and be able to fill the entire volume without immediately draining.

Similar performance to that of water only was achieved with the Class A and Class F foams agents. Class A foams offers improved extinguishment of Class A fires by providing deep penetration of the water into the burning material, due to its reduced surface tension compared to water. The Class F foam agent was an aqueous solution of high activity salts and stabilizers for use on oil, fat and grease related fires, as found in restaurant appliances such as deep fat fryers, griddles, chip pan hoods and ventilating equipment. The agent was a pre-mix, which eliminated the need for dilution before charging the system. The benefits of Class F foams for the protection of battery modules may be improved cooling abilities. A disadvantage could be the content of salts which may increase the likelihood of short-circuiting non-fire affected cells, as it is impossible to de-energize the cells. This is a feature that was not evaluated in these experiments, as only one cell was used.

The fire was promptly extinguished in two of the three nitrogen gas injection tests. However, the cooling of the Plate Thermometer device that was used to simulate an adjacent battery cell was limited. For a practical application, the low heat capacity of nitrogen gas would call for a pro-longed discharge or sequential discharges over a period of time that allow the fire and heated material to cool down. Additionally, the integrity of a battery module is an important parameter for maintaining a low oxygen concentration over a long time. The use of self-closing over-pressure vents on battery modules protected by an inert gas system should be considered. Preferably the vent should either go straight to the outside or be ducted to the outside. If this is not practical, it may be possible to vent to the surrounding room as long as the room is considerably (in the order of 10 times) larger than the volume of the module being protected. For the test where fire extinguishment failed, the connection point of the hose line was at the top of the simulated battery module. The nitrogen gas was not able to penetrate through the perforated steel sheet plates at the top of the module in this case, as no specific nozzle was available for the test that could provide enough momentum for the gas to reach the cell. It is likely that the gas escaped though the top gap around the perimeter of the module instead of filling the module.

When using CAFS, the simulated battery module was rapidly filled with foam in two of the three tests. This resulted in fire extinguishment and the cooling of the Plate Thermometer device that was used to simulate an adjacent battery cell was comparable to the tests with water discharging 5.0 liter/min. In one test, the foam was not able to fill the module and the fire was not extinguished. This experience highlights that the foam quality is essential in order to fill-up an obstructed volume and to overcome any internal pressure generated by a fire. As CAFS contains a considerable (per volume) amount of air, a self-closing over pressure vent may be required to allow the foam to enter the module. Like nitrogen gas, the limited cooling capacity observed in the tests calls for a pro-longed discharge or sequential discharges over a period of time, to allow the fire and heated materials to cool down.

One test was conducted with an Aqueous Vermiculite Dispersion (AVD) agent. According to the manufacturer, AVD is non-flammable and has excellent thermal insulation properties. When applied, it creates a film over the top of the fire. The film instantly dries to produce a non-flammable oxygen barrier. The AVD agent was applied at the top of the

simulated battery module but did not, due to its higher viscosity, penetrate the perforated horizontal steel sheet plates as fast as the other tested agents. The fire was fully extinguished once the cell was completely covered by the agent. However, the time to extinguish the battery cell took longer time with AVD than with the other agents and therefore the temperature of the Plate Thermometer was higher. In order to get AVD to more effectively pass through and around obstructions inside a battery casing or module, another application nozzle and probably a lower viscosity would be required.

9 Conclusion

Fire extinguishing tests were conducted inside a test compartment having a volume of approximately 33 m³, intending to simulate a battery room. A small cubic box made from steel sheets simulated a battery module inside the compartment. A commercially available Li-ion battery cell with a nominal capacity of 20 Ah was positioned at the bottom of the simulated battery module. The cell was of pouch type and had a carbon anode, a lithium iron-phosphate (LFP), LiFePO₄, cathode and an organic electrolyte. Fire was initiated by heating the cell from underneath with an electric heating element. This led to a temperature increase, bursting of the pouch envelope of the cell and release of combustible gases, which were ignited by a pilot flame inside the module. A temperature measurement device, the Plate Thermometer was positioned directly above the cell. This device simulated an adjacent cell and the temperature measurement provided an indication of how well a fire extinguishing agent would suppress or extinguish a fire and reduce heat exposure from the burning cell to adjacent cells.

The tests were designed to demonstrate the performance differences of total compartment water spray and water mist systems versus direct agent injection into the battery module as well as a comparison of the performance of different fire extinguishing agents.

The tests indicated that fire extinguishment of a battery cell fire inside a battery module is unlikely when using total compartment water spray or water mist fire protection systems. The water droplets are simply not able to get inside the battery module and reach the seat of the fire. It should, however, be recognized that a total compartment water spray or water mist fire protection system may well be used for the protection of battery rooms with the objective to reduce the probability of fire spread from the battery room to adjacent structures.

It was not possible to conduct any gaseous total flooding test within the project. It is possible that a gaseous agent could reach inside a battery module or casing depending on its system design, but this needs to be verified and the potential drawbacks with limited cooling from a gaseous agent must also be considered.

Direct injection of the fire extinguishing agent into the battery module to be protected is more effective but requires a fire- or gas- detection system that is able to identify the battery module where the fire is developing. It also requires that the fire protection system is sectioned such that the agent can be applied into the specific battery module. The tests conducted in this series of tests showed that agents with a high heat capacity (such as water and low-expansion foam) can provide rapid cooling and fire extinguishment. A reduced water tension may improve the possibilities for water penetration, whilst agents with a high viscosity may not be able to distribute properly inside the module to the seat of the fire. Agents with less heat capacity (such as high-expansion foam and nitrogen gas) will provide less cooling than plain water but fire extinguishment may be achieved if the system is designed correctly.

The tests reported here do not evaluate all aspects of extinguishment of Li-ion battery fires and mitigation of thermal runaway propagation. They only indicate some basic differences between application methods and fire extinguishing agents. A well-founded design of a fire extinguishing system requires a case by case evaluation of the specific

battery casing or module and integration with the Battery Management System. This can improve the possibilities for full fire extinguishment or at least prevent or limit fire propagation to further cells. The tests in this report provide a starting point for the type of systems, agents and application methods that can be useful for Li-ion battery fire extinguishment.

References

- [1] P. Andersson, J. Wikman, M. Arvidson, F. Larsson, O. Willstrand, “Safe introduction of battery propulsion at sea” RISE Research Institutes of Sweden, SP Rapport 2017:34, Borås 2017
- [2] F. Larsson, “Lithium-ion Battery Safety - Assessment by Abuse Testing, Fluoride Gas Emissions and Fire Propagation”, PhD Thesis, ISBN: 978-91-7597-612-9, Chalmers University of Technology, Göteborg, Sweden, **2017**. Available online: <http://publications.lib.chalmers.se/records/fulltext/251352/251352.pdf>
- [3] D. Doughty, E. P. Roth, “A general discussion of Li ion battery safety“, *The Electrochemical Society Interface*, summer 2012, 37-44, **2012**.
- [4] F. Larsson, P. Andersson, B.-E. Mellander, “Lithium-Ion Battery Aspects on Fires in Electrified Vehicles on the Basis of Experimental Abuse Tests”, *Batteries*, 2, 9, **2016**.
- [5] F. Larsson, P. Andersson, P. Blomqvist, B.-E. Mellander, “Toxic fluoride gas emissions from lithium-ion battery fires”, *Scientific Reports*, 7, article number 10018, **2017**. Available online: <https://www.nature.com/articles/s41598-017-09784-z>
- [6] F. Larsson, P. Andersson, P. Blomqvist, A. Lorén, B.-E. Mellander, “Characteristics of Lithium-ion batteries during fire tests”, *Journal of Power Sources*, 271, 414–420, **2014**.
- [7] F. Larsson, P. Andersson, P. Blomqvist, B.-E. Mellander, “Gas emissions from Lithium-ion battery cells undergoing abuse from external fire”, Conference proceedings of Fires in vehicles (FIVE) 2016, Baltimore, 5-6 October 2016, edited by P. Andersson, B. Sundström, *SP Technical Research Institute of Sweden*, Borås, Sweden, p. 253-256, **2016**.
- [8] P. Ribière, S. Grugeon, M. Morcrette, S. Boyanov, S. Laruelle, G. Marlair, “Investigation on the fire-induced hazards of Li-ion battery cells by fire calorimetry”, *Energy Environmental Science*, 5, 5271-5280, **2012**.
- [9] A. Lecocq, G. G. Eshetu, S. Grugeon, N. Martin, S. Laruelle, G. Marlair, “Scenario-based prediction of Li-ion batteries fire-induced toxicity“, *Journal of Power Sources*, 316, 197-206, **2016**.
- [10] P. Andersson, P. Blomqvist, A. Loren, F. Larsson, “Using Fourier transform infrared spectroscopy to determine toxic gases in fires with lithium-ion batteries”, *Fire and Materials*, 40, 999–1015, **2016**.
- [11] P. Andersson, P. Blomqvist, A. Lorén, F. Larsson, “Investigation of fire emissions from Li-ion batteries”, SP Report 2013:5, *SP Technical Research Institute of Sweden*, Borås, Sweden, ISBN 978-91-87461-00-2, **2013**.

- [12] N. P. Lebedeva, L. Boon-Bretz, "Considerations on the Chemical Toxicity of Contemporary Li-Ion Battery Electrolytes and Their Components", *Journal of The Electrochemical Society*, 163 (6), A821-A830, **2016**.
- [13] A. W. Golubkov, S. Scheikl, R. Planteu, G. Voitic, H. Wiltse, C. Stangl, G. Fauler, A. Thaler, V. Hacker, "Thermal runaway of commercial 18650 Li-ion batteries with LFP and NCA cathodes – impact of state of charge and overcharge", *RSC Adv.*, 5, 57171-57186, **2015**.
- [14] A. Hammami, N. Raymond, M. Armand, "Runaway risk of forming toxic compounds", *Nature*, 424, 635-636, **2003**.
- [15] Z. Chen, Y. Qin, Y. Ren, W. Lu, C. Orendorff, E. P. Roth, K. Amine, "Multi-scale study of thermal stability of lithiated graphite", *Energy Environmental Science*, 4, 4023-4030, **2011**.
- [16] Q. Wang, P. Ping, X. Zhao, G. Chu, J. Sun, C. Chen, "Thermal runaway caused fire and explosion of lithium ion battery", *Journal of Power Sources*, 208, 210-214, **2012**.
- [17] F. Larsson, J. Andersson, P. Andersson, B.-E. Mellander, "Thermal modelling of cell-to-cell fire propagation and cascading thermal runaway failure effects for lithium-ion battery cells and modules using fire walls", *Journal of the Electrochemical Society*, 163, A2854–A2865, **2016**.
- [18] C. F. Lopez, J. A. Jeevarajan, P. P. Mukherjee, "Experimental analysis of thermal runaway and propagation in lithium-ion battery modules", *Journal of the Electrochemical Society*, 162 (9), A1905-A1915, **2015**.
- [19] J. Lamb, C. J. Orendorff, L. A. M. Steele, S. W. Spangler, "Failure propagation in multi-cell lithium-ion batteries", *Journal of Power Sources*, 283, 517-523, **2015**.
- [20] F. Larsson, B.-E. Mellander, "Lithium-ion Batteries used in Electrified Vehicles – General Risk Assessment and Construction Guidelines from a Fire and Gas Release Perspective", *RISE Research Institutes of Sweden*, Sweden, Borås, SP Rapport 2017:41, ISSN 0284-5172, **2017**.
- [21] D. Hill, "Final Report, Considerations for ESS Fire Safety", Consolidated Edison, New York, NY, Report No.: OAPUS301WIKO(PP151894), *DNV GL*, Rev. 3, January 18, **2017**.
- [22] F. Larsson, S. Bertilsson, M. Furlani, I. Albinsson, B.-E. Mellander, "Gas explosions and thermal runaways during external heating abuse of commercial lithium-ion graphite-LiCoO₂ cells with different levels of ageing", *Journal of Power Sources*, Vol. 373, p. 220-231, **2018**.

Appendix A - Results

The tests were evaluated based on temperature readings of a Plate Thermometer mimicking a neighboring cell. These readings were compared with the readings of the Plate Thermometer in three free-burning tests. In order to compare the different tests, the signals were time-shifted so that the voltage drop coincided. Figures A.1 and A.2, respectively, shows the results after the time shift for the free-burn tests.

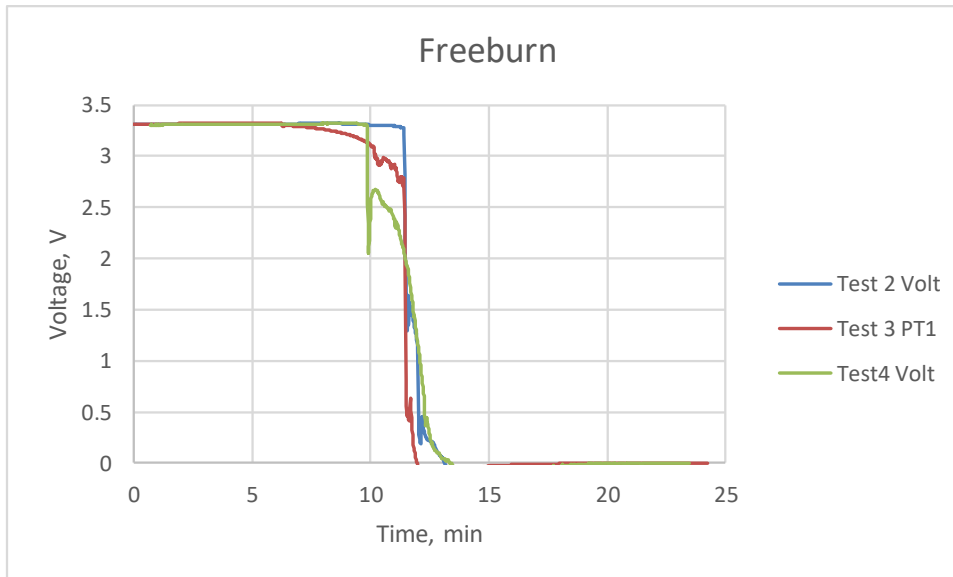


Figure A.1 Time shifted voltage signals for the free-burn tests.

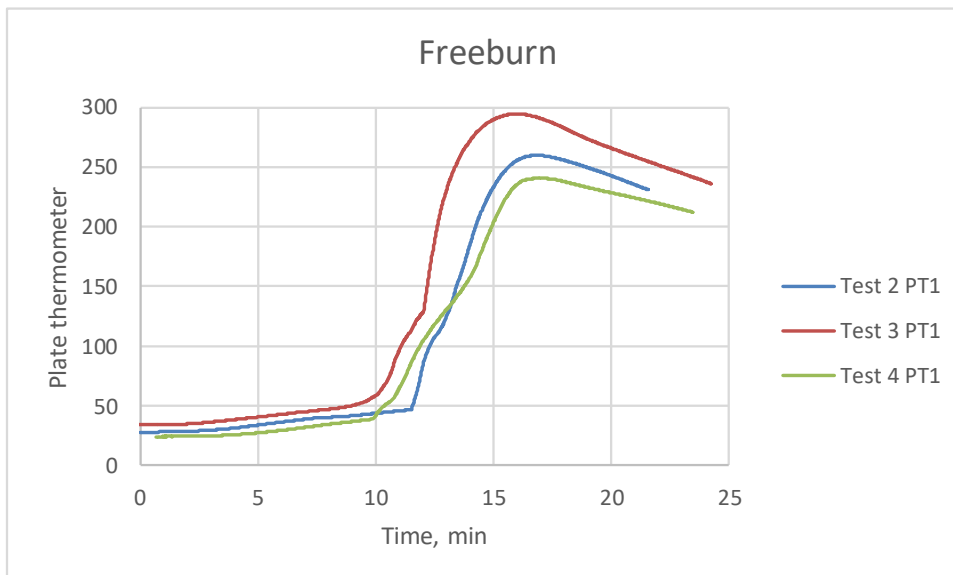


Figure A.2. Time shifted Plate Thermometer signals for the free-burn tests.

Temperature readings of a thermocouple tree was conducted in all tests, the temperature increase in the room was, however, very limited as seen in Figure A.3 and these readings were therefore not used for the analysis.

Temperature recordings were also made on the cell surface facing downwards and upwards in the experimental set-up. These recording were merely used to check that the

set-up worked and are therefore not presented further here, an example of such readings is presented in Figure A.4.

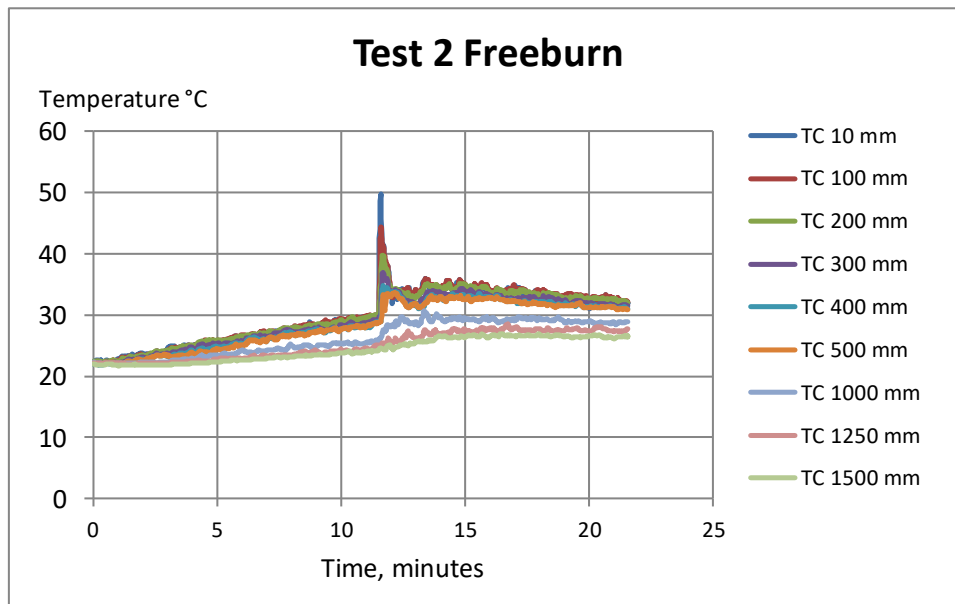


Figure A.3 Temperature readings TC tree inside the test compartment in free-burn fire test.

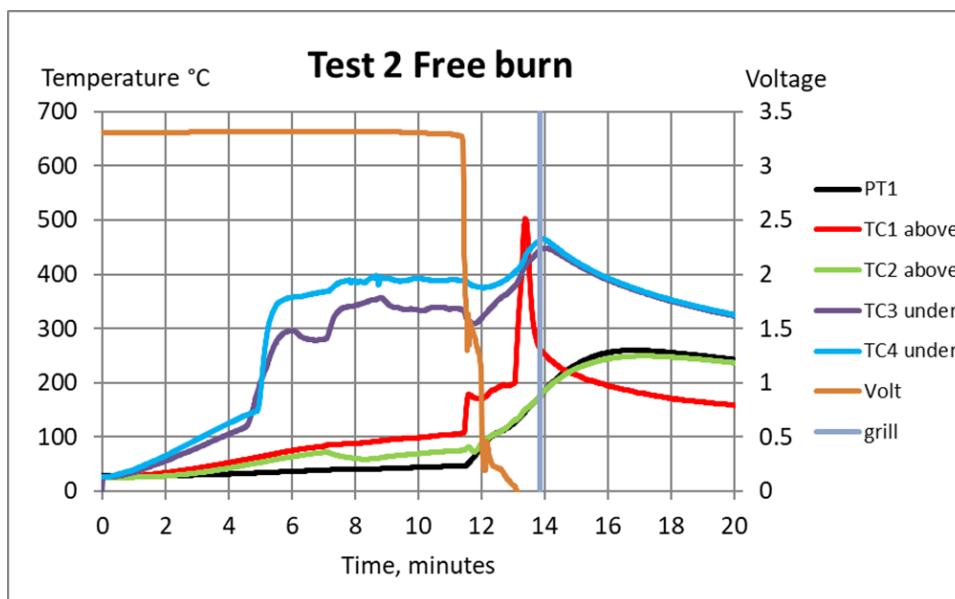


Figure A.4. All measurements conducted at and in the vicinity of the cell. The time when the electric heating element was turned off also indicated as “grill” 14 minutes.

Total compartment system results

The time shifted results for the water spray, low-pressure water mist and high-pressure water mist total compartment systems are presented in Figures A.5, A.6 and A.7, respectively. The time for activation of the extinguishing system/voltage drop is indicated in the figures as “activate”. As can be seen the none of the extinguishing systems influenced the temperature progress. Some limited influence can be seen only due to that excessive amount of water was accumulating on the insulation boards underneath the cell.

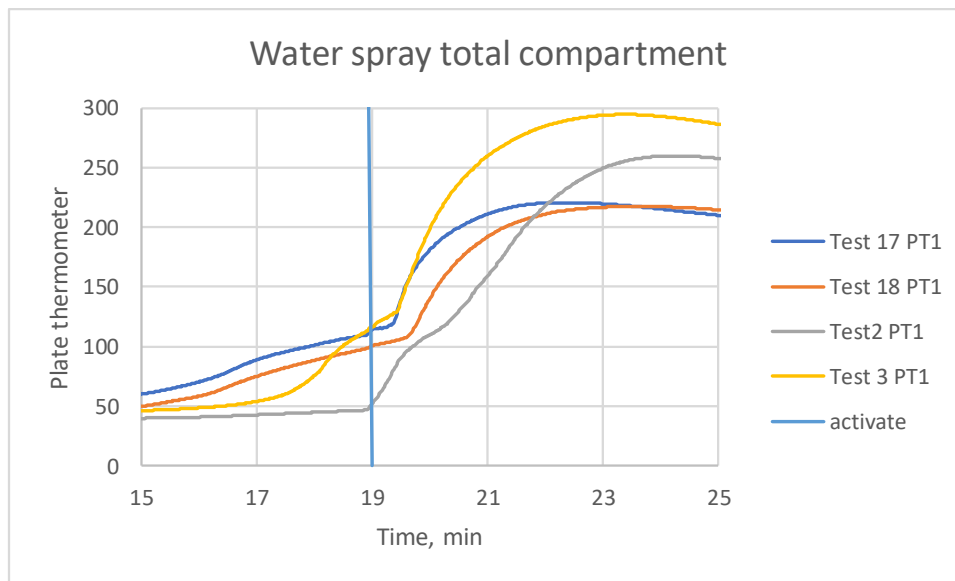


Figure A.5 Plate Thermometer readings in the water spray total compartment system tests compared with the readings from the free-burn tests.

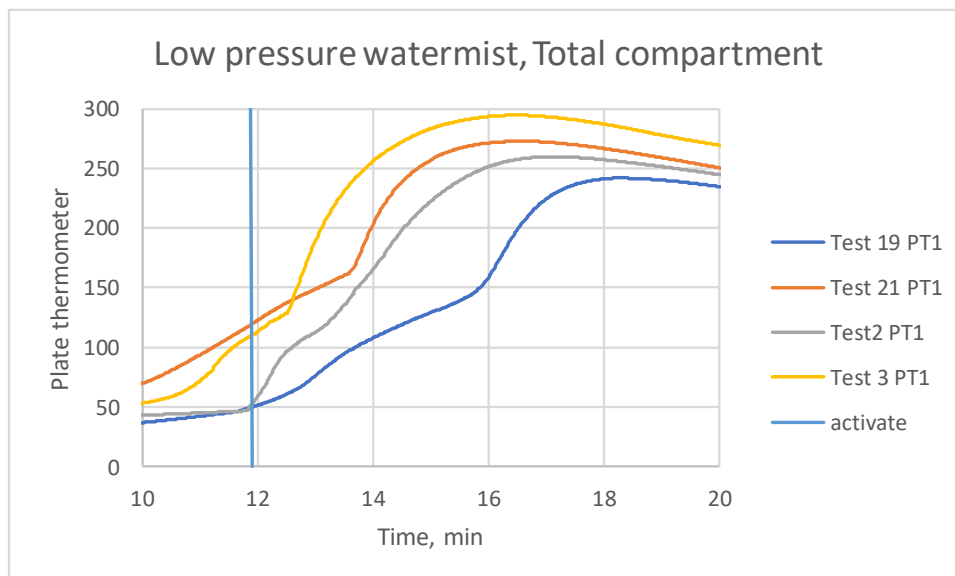


Figure A.6 Plate Thermometer readings in the low-pressure water mist total compartment system tests compared with the readings from the free-burn tests.

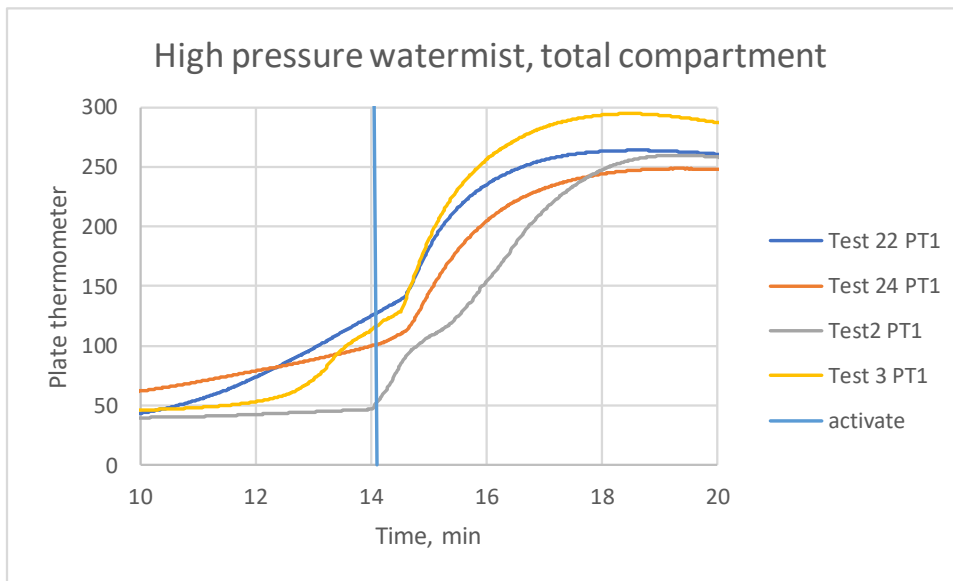


Figure A.7. Plate Thermometer readings in the high-pressure water mist total compartment system tests compared with the readings from the free-burn tests.

Direct injection tests

The Plate Thermometer readings in the direct injection tests using water spray, Class A foam, Class F foam, CAFS, nitrogen and AVD extinguishing agents are presented in Figures A.8 through A.14, respectively.

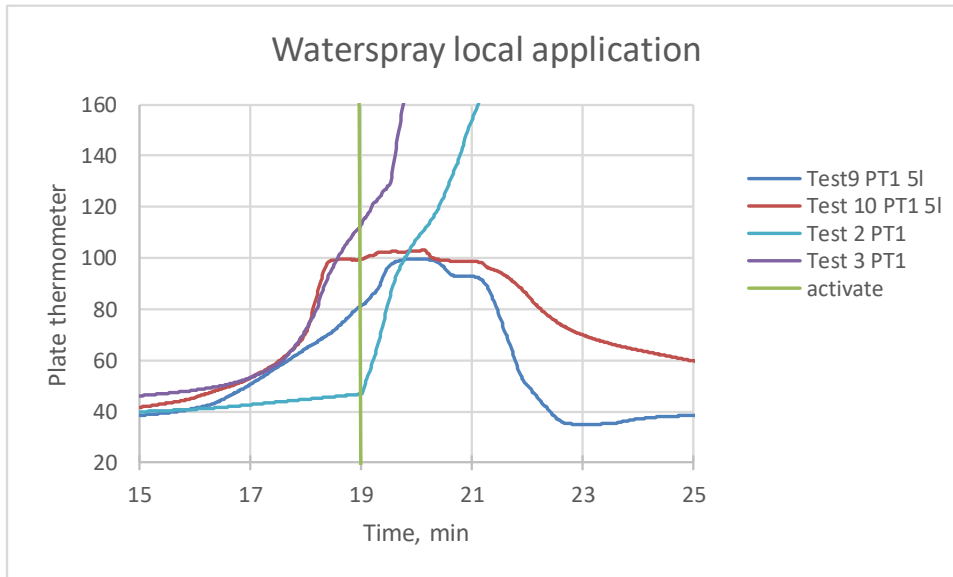


Figure A.8. Full cone water spray direct injection tests.

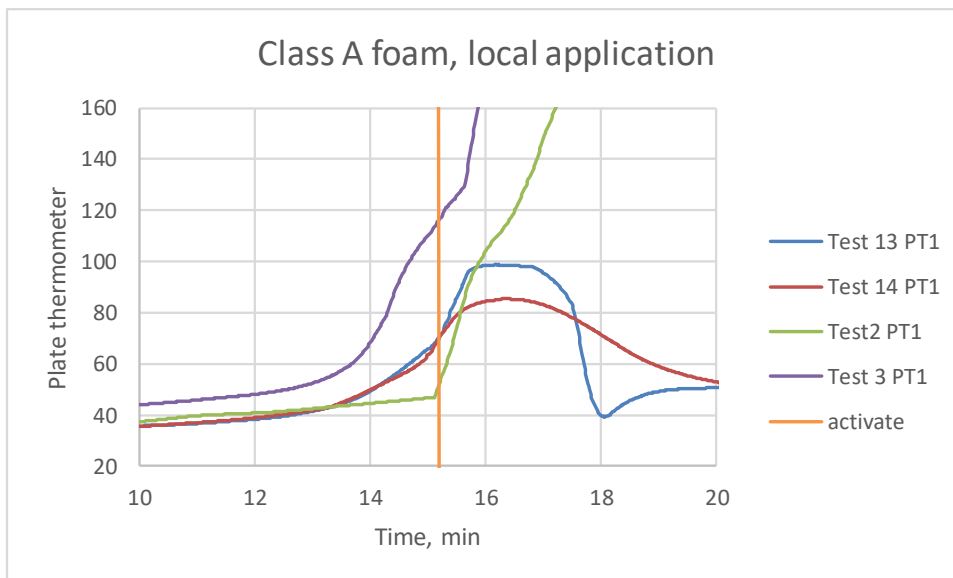


Figure A.9. Class A foam direct injection tests.

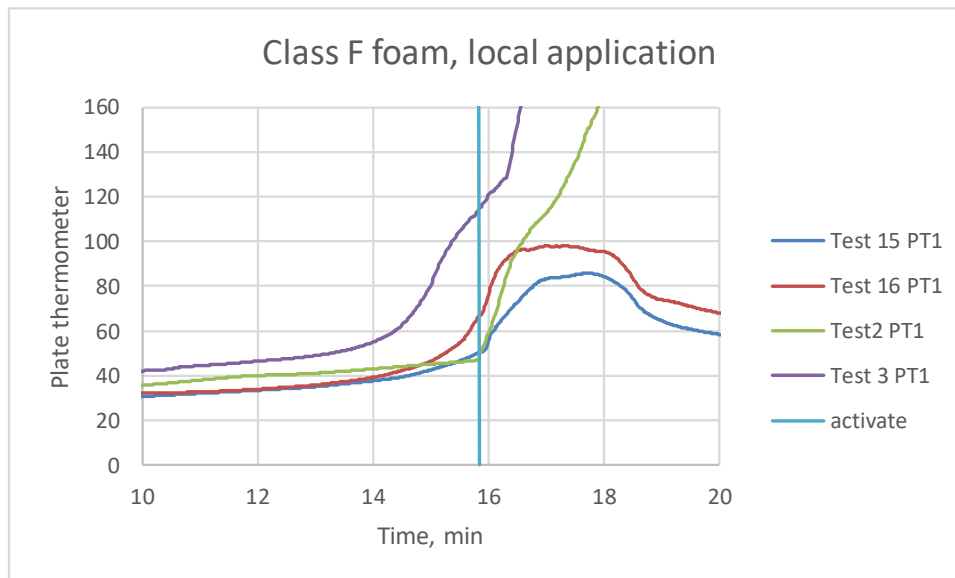


Figure A.10. Class F foam direct injection tests.

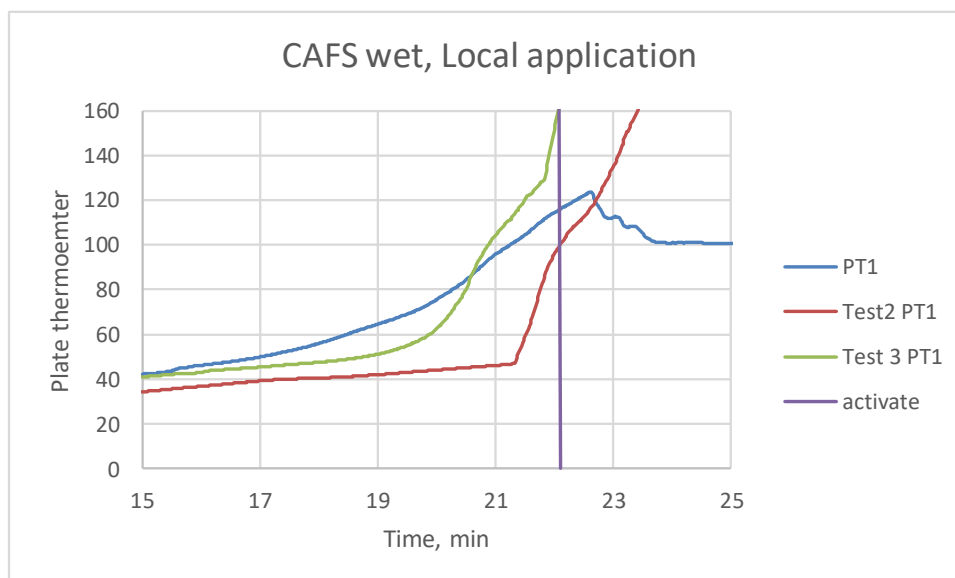


Figure A.11. “Wet” CAFS direct injection test. In this test, the fire did not start until one minute after the voltage drop occurred, this is why the activate line does not coincide with the “knee” in Test 2.

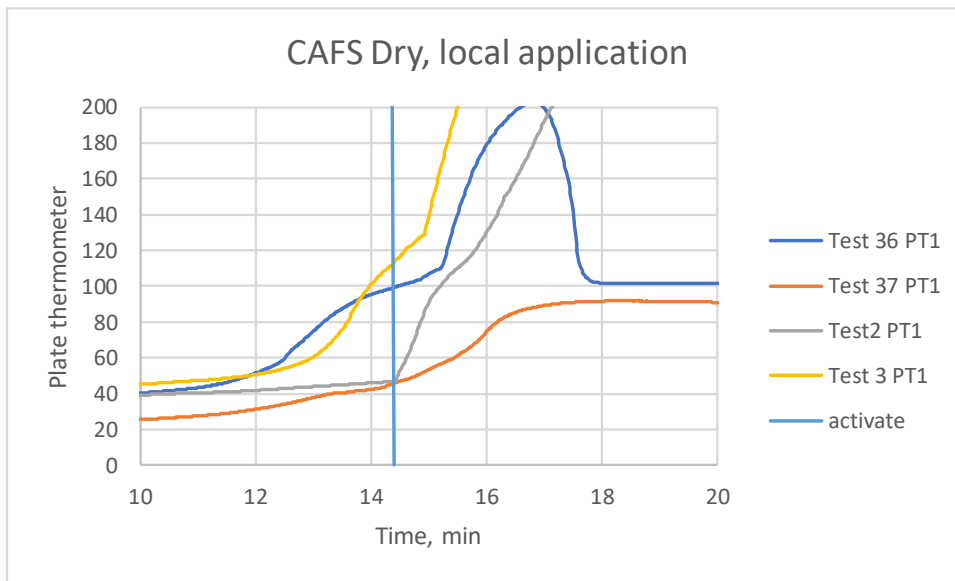


Figure A.12. “Dry” CAFS direct injection tests. For Test 36 there was no fire extinguishment due to the foam.

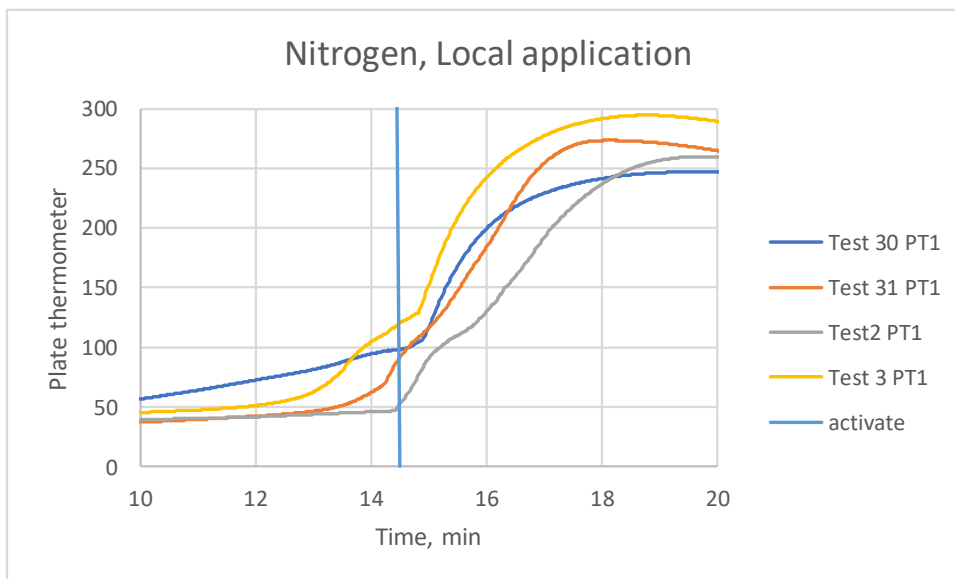


Figure A.13. Nitrogen direct injection tests. For these tests, the flames were extinguished about one minute after the nitrogen was released. As can be seen, there was still no reduction in peak temperature of the Plate Thermometer temperature compared to the free-burn tests.

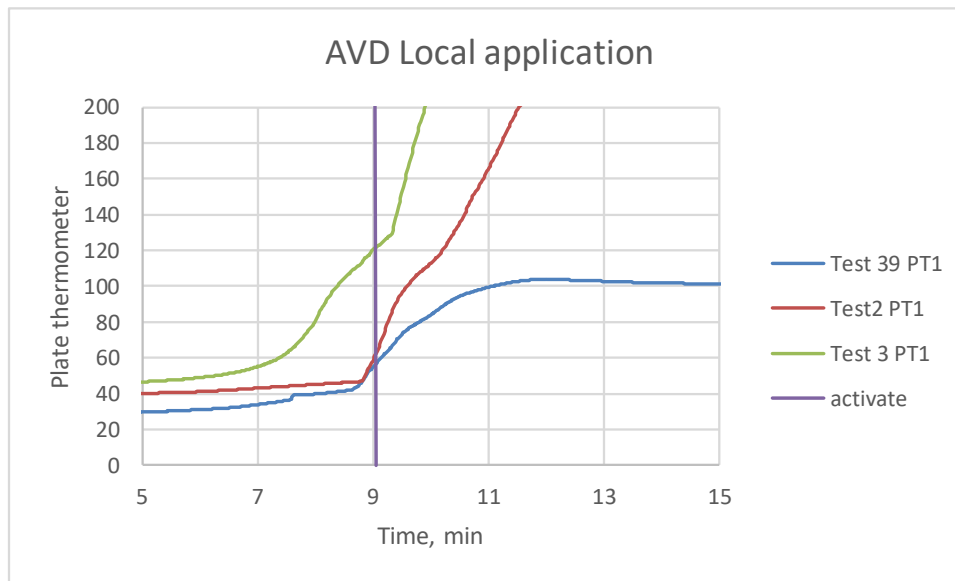


Figure A.14. AVD direct injection test

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